Effects of microwave dielectric heating on heterogeneous catalysis

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The effect of microwave dielectric heating on both endothermic and exothermic reactions was investigated. Apparent equilibrium shifts for both reactions were observed which were attributed to the formation of spatial hot spots in the catalyst bed. The possible location of remarkable temperature gradients was examined experimentally and theoretically.

KEY WORDS: hydrogen sulfide decomposition; thiophene hydrodesulfurization; microwave dielectric heating; hot spots.

1. Introduction

The influence of microwave dielectric heating on catalytic systems involving solid catalysts has been studied intensively in recent years, and there have been numerous reports that for some chemical reactions the rates are accelerated and in others the product selectivity is changed when microwave radiation is used rather than conventional heating [1–6]. Whether this is simply due to the faster, selective dielectric heating provided by microwaves, or whether there is any specific microwave effect, have been the subjects of much discussion. Two models of the mechanism of microwave-assisted chemical reactions have been proposed to interpret the observations, namely thermal effects and non-thermal effects. Thermal effects are those resulting from dielectric heating which may cause a different temperature regime. Non-thermal effects are the specific effects resulting from non-thermal interactions between the substrates and microwave irradiation and are not caused by different temperature regimes.

In the early studies on microwave-assisted catalysis, the results that could not be explained solely as a consequence of simple thermal heating led to the suggestions of a non-thermal microwave-specific effect [7–9]. However, further studies both theoretically and experimentally have conclusively demonstrated that the specific athermal effects are implausible. Stuerga and Gaillard [10,11] theoretically analyzed the interaction between microwave electromagnetic fields and heated chemicals and finally concluded that the microwave field cannot have any molecular or athermal effects on chemicals. Hajek [12] experimentally investigated microwave-assisted catalytic reactions from the point of view of

the activation of chemical reactions and excluded the existence of the non-thermal effect in both homogeneous and heterogeneous reactions.

Thus, the majority of the reaction rate and product selectivity enhancements under microwave conditions can only be attributed to thermal or temperature effects which may result because of differences between the real reaction temperature at the reaction sites and the observed average temperature. In a gas/solid heterogeneous catalytic system, this temperature difference may exist in different regimes within the heterogeneous system, and there are three cases to be considered. (i) The catalyst particle temperature and/or catalyst support temperature are different from the gas temperature. For the oxidative coupling of methane under microwave irradiation, Roussy *et al.* [13] proposed that the gas was colder than the catalyst bed under microwave irradiation to interpret the enhancement in the selective formation of higher hydrocarbons. (ii) The catalyst particle temperature is higher than the catalyst support temperature. Chemat *et al.* [14] investigated heterogeneous catalysis reactions using a continuous microwave reactor and compared the results to those obtained by conventional heating. The increased reaction rate was attributed to selective heating of the catalyst particles. The temperature of the reactive site was then calculated to be 9–18 K above the bulk temperature. Thomas [15] used heat transfer analysis to determine the potential for selective heating of metallic catalyst particles attached to a support through the use of microwaves. It was concluded that selective heating is possible with microwave fields of high frequency heating catalyst beds cooled by a gas at low pressure. This selective heating was found to have a strong dependence on catalyst particle size and on microwave frequency. (iii) The temperature of the spatial hot spot within the catalyst bed is different from the average temperature of the catalyst bed. After investigating the oxidative coupling of methane under microwave conditions,

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Bond et al. [16] and Chen et al. [17] both suggested the presence of such "hot spots" in the catalytic beds.

Clearly, comparative studies on microwave and conventional effects on reactions must be based on reliable temperature measurements. However, the direct measurement of temperature under conditions where there are strong electromagnetic fields is problematical, but may be overcome, for example, by using optical fiber technology, although such measurements are still only capable of providing average temperatures.

The aim of the present study was to obtain further understanding of the thermal or temperature effect of microwave dielectric heating on gas/solid heterogeneous catalytic systems by examining both endothermic and exothermic reactions under microwave conditions. By experimentally investigating the effect of the inlet gas temperature and theoretically analyzing the heat transfer system the possible location of the proposed spatial hot spots was also studied.

The endothermic reaction selected for this study was the decomposition of hydrogen sulfide into hydrogen and sulfur. The basic reaction is given by

$$H_2S \rightleftharpoons H_2 + \tfrac{1}{2}S_2 \qquad \Delta H^o = 84.8 \, kJ \, mol^{-1} \qquad (1)$$

with negligible production of other gaseous sulfur species [18,19].

The related exothermic reaction selected for this study was the hydrodesulfurization of thiophene where thiophene reacts with hydrogen to produce butane and hydrogen sulfide:

$$C_4H_4S + 4H_2 \rightleftharpoons C_4H_{10} + H_2S$$
$$\Delta H^o = -262.6 \, kJ \, mol^{-1}. \qquad (2)$$
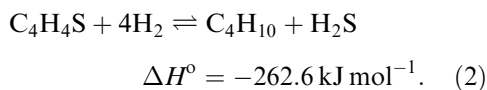
2. Experimental

All reactions were carried out in a laboratory-scale continuous-flow reaction system with a tubular packed-bed quartz reactor (i.d. $10 \times$ length 150 mm) which could be placed in either a cylindrical microwave cavity or a conventional tubular furnace under atmospheric pressure [4]. The feed gas could be heated using a heating tape along the tube prior to the reactors, if appropriate. In the microwave heating system, a directional coupler was inserted into the coaxial microwave guide so that the amount of the microwave power reflected from the cavity could be measured. This was minimized by tuning the microwave cavity with two adjustable stubs. The temperature of the catalyst was measured with an Accufiber optical fiber thermometer system (Model 100C, LUXTRON). The optical sensor (o.d. 1.27 mm, Model 900-LP-12SS, LUXTRON) was made of sapphire which is "transparent" to microwaves.

Hydrogen sulfide (99.5%), hydrogen (99.99%), thiophene (99%) and molybdenum disulfide (99%, particle diameter 2 μm) were supplied by Aldrich. γ-Al$_2$O$_3$ (99% Al$_2$O$_3$, surface area 90 m^2/g and ammonium heptamolybdate [(NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O] (99%) were supplied by Johnson Matthey. The catalysts used for the decomposition of hydrogen sulfide were prepared either by mechanical mixing or by wet impregnation, according to the procedures described previously [4]. The mechanically mixed catalyst was made by mixing 30 wt% MoS$_2$ (2 μm) with 70 wt% alumina (66 μm), then compressing the mixture into pellets, followed by grinding and sieving to the desired size (152–178 μm). Co/Mo/Al$_2$O$_3$ hydrotreating catalyst C2634, a commercial catalyst used in industry, was provided by BP, and ground to 152–178 μm before use. The catalyst was presulfided in a mixture of 15 mol% H$_2$S in H$_2$ at a temperature of 400 °C for 2 h in a conventional tubular furnace before the hydrodesulfurization reaction. The conversion of hydrogen sulfide or thiophene was defined as the percentage of its disappearance measured by an on-line quadrupole mass spectrometer.

3. Results and discussion

3.1. Effects of microwave dielectric heating on the endothermic decomposition of H$_2$S

When 0.482 g of impregnated MoS$_2$/γ-Al$_2$O$_3$ catalyst was used with a H$_2$S stream flow rate of 31 ml/min at atmospheric pressure, it was observed using the quadrupole mass spectrometer that the conversion of H$_2$S could be maintained at a constant level when the reaction temperature was kept constant. These conditions could be reproduced at different temperature. The H$_2$S conversion levels as a function of temperature are shown in figure 1 for both microwave and conventional heating experiments.

Figure 1 shows that the H$_2$S conversion increased with temperature, reaching 12 mol% at 800 °C. In contrast, the H$_2$S conversion obtained with conventional heating was only 6.5 mol% at 800 °C. Figure 1 also shows the theoretical H$_2$S conversion at equilibrium, based on thermodynamic data [18,19]. It is significant that the results obtained under conventional heating conditions were in close agreement with the equilibrium data. However, the H$_2$S conversion under microwave conditions was much higher than that obtained with conventional heating at the same temperature. Most surprisingly, the H$_2$S conversions were higher than the theoretical equilibrium H$_2$S conversions. This suggested that the reaction temperature at some sites in the catalyst bed was much higher than the average temperature measured. These higher temperature sites or points are usually referred to as "hot spots" [16,17].

Such hot spots may be created by the difference in dielectric properties of materials, by the uneven distribution of electromagnetic field strength, or by the volumetric dielectric heating under microwave conditions
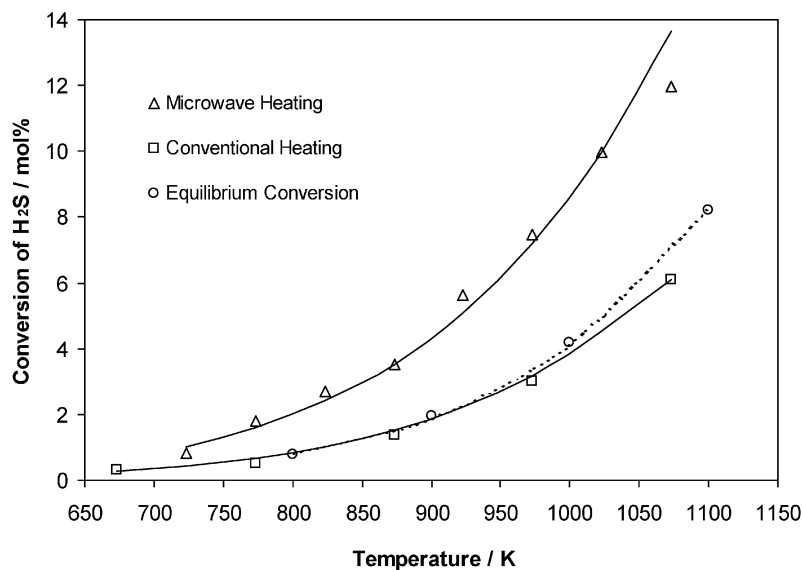
Figure 1. Conversion of hydrogen sulfide as a function of temperature.

[20]. The most significant point is that this local over-heating is not detectable since only average temperature is measured unless multiple probes or infrared tomography is used.

3.2. Effects of microwave dielectric heating on the exothermic hydrodesulfurization (HDS) of thiophene

Thermodynamic data of the hydrodesulfurization (HDS) of thiophene shows that this reaction is a strongly exothermic process and the reaction has a large negative free energy change at low temperatures [21]. Thus, increasing the reaction temperature could in principle limit the conversion of thiophene. Based on the "hot spots" assumption the reaction temperature at some points should be higher than that measured, which has

the consequence that (a) the rate of the forward reaction should be increased, but (b) the maximum attainable conversion should be decreased provided that the reaction rate is high enough to reach the equilibrium conversion.

The experiment was carried out for the exothermic HDS reaction at different temperature levels subject to microwave dielectric heating where 7 vol% thiophene was present in the inlet gas stream. The total gas flow rate was kept at 40 ml/min under atmospheric pressure and 0.5 g C2634 catalyst was used. The experiment was also carried out with conventional heating under identical conditions for comparison. The results are presented in figure 2.

It is seen that the variation of the conversion of thiophene with temperature occurred in three stages,
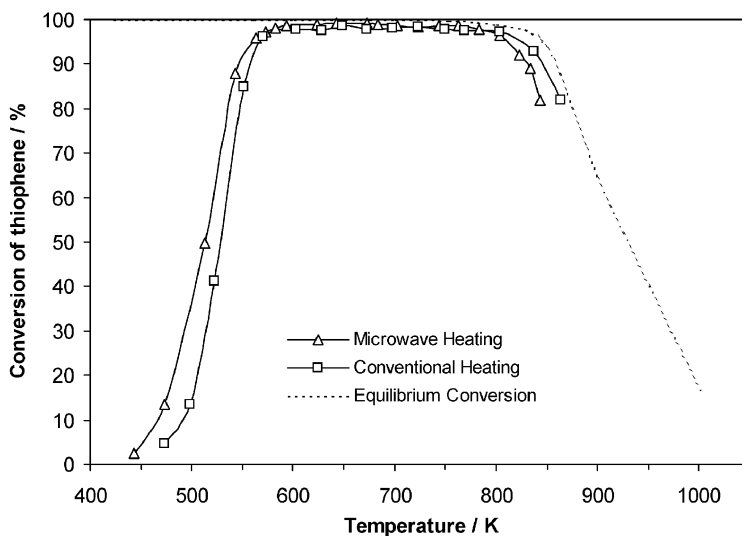

Figure 2. Conversion of thiophene as a function of temperature.

both under microwave conditions and with conventional heating. In the lower temperature range, the conversion of thiophene increased markedly with temperature up to 300 °C. Then, the conversion reached a very high level, approaching the equilibrium conversion, in the temperature range 300–500 °C. This high level of conversion was followed by a decline after the temperature was increased above 500 °C.

Figure 2 also shows the theoretical conversion of thiophene at equilibrium, calculated as described below. If x is the mole fraction of thiophene that reacts with hydrogen at equilibrium, and the reaction is started with the mixture of thiophene and hydrogen containing 7 mol% of thiophene, the equilibrium constant K_p can be represented as:

$$K_p = \frac{p_{\text{butane}} \, p_{\text{H}_2\text{S}}}{p_{\text{thiophene}} \, p_{\text{H}_2}^4} = \frac{x^2(14.28 - 3x)^3}{(1 - x)(13.28 - 4x)^4} \qquad (3)$$

where p is the partial pressure. Knowing the equilibrium constants at different temperature levels, which can be obtained from the following equation based on the thermodynamic data [21,22], values of x can be calculated:

$$\Delta G_f^o = -RT \ln K_p, \qquad R = 8.314 \, \text{J} \, \text{mol}^{-1} \, \text{K}^{-1}. \quad (4)$$

It is important to note the difference in thiophene conversions obtained using the two heating methods. In the first stage, the reaction rate under microwave conditions was higher than that with conventional heating. This observation indicated that the reaction temperature was higher than that measured while the reaction was under kinetic control. In the second stage, the thiophene conversion approached the equilibrium value which is close to 100% and there was no significant difference in thiophene conversions by the two heating methods. This result also showed a high catalytic activity of the commercial catalyst C2634. In the high-temperature range, i.e., the third stage, when the temperature was increased further the conversion decreased, limited by the equilibrium conversion. It is interesting to note that in this higher temperature range, under microwave conditions the thiophene conversion diverged more from the theoretical equilibrium data. By contrast the thiophene conversion with conventional heating remained close to the theoretical curve. Based on the hot-spot assumption, the reaction temperature was higher under microwave conditions than that measured. Furthermore, provided that the rate-determining step for both forward and back reactions occurs between adsorbed species that are fully accommodated to the active catalyst temperature the equilibrium that is set up will be characteristic of the hot-spot temperature and not the average temperature of the catalyst bed as a whole. Thus, for this exothermic reaction—hydrodesulfurization of thiophene—the hot spots could increase the reaction rate, but they could also "shift" the equilibrium in a less favorable direction, because the equilibrium constant at

the temperature of the hot spots was lower than that at the apparent measured temperature in the bulk matter.

It was difficult to study the HDS reaction at higher temperatures under atmospheric pressure conditions because of the thermocracking of thiophene at higher temperatures (>600 °C), which results in a change in the product distribution and C_1, C_2 hydrocarbon products are produced.

3.3. Studies on the possible location of the remarkable temperature gradient

As discussed previously, there may be three kinds of temperature variation in the heterogeneous catalytic system which might explain the difference between the reaction temperature and the average temperature measured. These were investigated further by both experiments and theoretical analysis, and are described below.

3.3.1. Effects of varying inlet gas temperature

Because of the large dielectric loss difference between MoS_2 and γ-Al_2O_3, the MoS_2 particles may absorb microwave energy at a substantially higher rate than the surrounding γ-Al_2O_3 particles [23]. So, there is the possibility of establishing a temperature gradient from the reaction surface to the gas phase. In this case, varying the gas-phase temperature could change the temperature gradient, thus affecting the reaction rate under these conditions.

Figure 3 compares the results of H_2S conversion under microwave heating conditions with and without the reactant gas being pre-heated to 230 °C before it reached the reactor. The reaction was carried out at two reaction temperature levels at a flow rate of 31 ml/min H_2S under atmospheric pressure using 0.482 g mechanically mixed catalyst MoS_2 (30 wt%) + γ-Al_2O_3 (70 wt%). It can be seen from the results that there was no significant difference in H_2S conversion between the runs with reactant gas pre-heating (up to 230 °C) and that without pre-heating, at bulk catalyst temperature of either 600 or 700 °C. This suggests that varying the gas-phase temperature does not change the temperature gradient, or affect the reaction rate.

It was also noted that the conversion of H_2S with the mechanically mixed catalyst was much higher than that obtained with the impregnated catalyst at the same temperature (see figure 1). With the conventional heating method, the impregnated catalyst with better dispersion of catalyst particles and higher surface area generally gives a better result compared to the mechanically mixed catalyst. Under microwave heating conditions, however, the latter was more likely to have a higher concentration of hot spots, or have a higher temperature of hot spots. Those hot spots that had higher temperatures for the reaction could result in a significant difference in H_2S conversion between the two catalysts used.
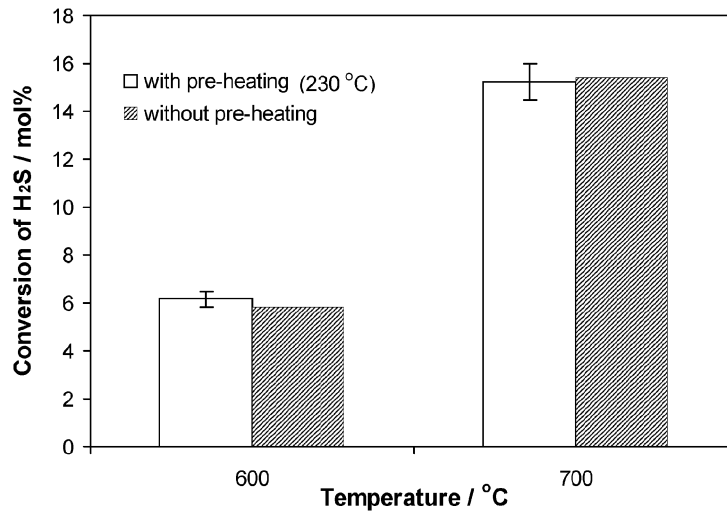
Figure 3. Effects of pre-heating of inlet reactant gas on the decomposition of H_2S.

3.3.2. Theoretical analysis of temperature difference between MoS_2 and alumina support

Heat transfer model. Following Perry *et al.* [24], a simplified model of heat transfer based on a MoS_2 particle suspended in gas at 1 atm pressure inside a spherical γ-Al_2O_3 cavity was employed to estimate the temperature difference between MoS_2 and its alumina support. It was proposed on the assumptions that (a) in a steady state, microwave energy absorbed by the MoS_2 particle is equal to the heat lost only into the gas phase, and (b) microwave energy is absorbed by MoS_2 whilst γ-Al_2O_3 support does not absorb a significant amount of microwave energy. These assumptions represent the best opportunity for a temperature gradient to be created, as the heat conduction into the γ-Al_2O_3 support would reduce the temperature gradient.

Microwave energy absorbed by each MoS_2 particle. The typical weight of the catalyst used is 0.50 g with 30 wt% MoS_2, so the weight of MoS_2 present is typically $0.50 \times 0.30 = 0.15$ g, and the volume of MoS_2 is $0.15/4.8 = 3.125 \times 10^{-2}$ cm^3 where the density of MoS_2 is 4800 kg m^{-3}. If each particle of MoS_2 is spherical and has a diameter of 0.2 μm for the supported catalyst, then the volume of each particle is $\pi D^3/6 = \pi 8 \times 10^{-15}/6$ cm$^3 = 4.189 \times 10^{-15}$ cm^3, and the number of the particles is $3.125 \times 10^{-2}/4.189 \times 10^{-15} = 7.46 \times 10^{12}$. Assuming that the alumina support does not absorb a significant amount of microwave energy and that the typical absorbed microwave energy is 60 W, the energy absorbed by each MoS_2 particle is equal to $60/7.46 \times 10^{12} = 8.043 \times 10^{-12}$ W.

Heat loss. Heat loss calculations suggest that hot spots are more likely to develop as the size of the particles increases by an order of magnitude. The following calculation represents this although it may not accurately reflect the extent of the temperature differential. Such calculations of course assume thermodynamic control and may not accurately reflect the time dependence of the phenomenon.

For a spherical MoS_2 particle of radius R_1 in a spherical γ-Al_2O_3 cavity of radius R_2 the rate of heat transfer is given by [24]

$$Q = A\left[\frac{1}{\alpha_1} + \left(\frac{R_1}{R_2}\right)\left(\frac{1}{\alpha_2} - 1\right)\right]^{-1}\left[\frac{P}{(2\pi MRT)^{1/2}}\right]$$
$$\times [(C_v + \tfrac{1}{2}R)(T_1 - T_2)] \tag{5}$$

when the mean free path of the gas exceeds the particle size. Here α_1 and α_2 are the accommodation coefficients of the gas-phase molecules at the surface of the particle and support wall, P is the gas pressure, M is the molecular weight, A is the particle surface area, and T_1 and T_2 are the temperatures of the particle and the support wall respectively. For systems where $R_2 \gg R_1$ this formula simplifies to

$$Q = A\alpha_1\left[\frac{P}{(2\pi MRT)^{1/2}}\right][(C_v + \tfrac{1}{2}R)(T_1 - T_2)]. \tag{6}$$

When $P = 1.013 \times 10^5$ Pa (1 atm), $M = 34 \times 10^{-3}$ kg mol^{-1} (H_2S), $\alpha_1 = 0.8$, $C_v = 34.2$ J mol^{-1} K^{-1} (H_2S), $R = 8.314$ J mol^{-1} K^{-1}, $T = 1000$ K and the particle surface area $= 1.257 \times 10^{-13}$ m^2, the heat loss from a MoS_2 particle is

$$Q = 1.257 \times 10^{-13} \times 0.8 \times 2.617 \times 10^3 \times 38.36$$
$$\times (T_1 - T_2)\, \text{J s}^{-1}$$
$$= 1.01 \times 10^{-8} \times (T_1 - T_2)\, \text{J s}^{-1}$$

Comparing this value with the heat generated by microwaves in each particle of 8.043×10^{-12} W, it can be concluded that the temperature difference between the MoS_2 particle and the alumina support is very small, i.e. about 8×10^{-4} K This limiting case (optimal heating) analysis indicates that the MoS_2 particles are

in thermal equilibrium with the surrounding γ-Al_2O_3 support. This result is in keeping with that of Perry *et al.* for a platinum–air–alumina system where the temperature difference between the metallic Pt particle and its alumina support is negligible, i.e. 1.1×10^{-10} K [25].

The calculation also shows that the diameter of the MoS_2 particles would have to be of the order of mm to achieve a significant temperature difference. Thus only hot spots of this size can be maintained for significant times in the catalyst because of the rapid transfer of heat via the gas phase. This estimation is in agreement with the heat transfer analysis for metallic catalysts attached to a support through the use of microwaves [15].

3.3.3. Existence of spatial hot spots

From the above experimental results and the theoretical analysis, a significant temperature difference between the catalyst and the bulk gas and between the MoS_2 particle and the γ-Al_2O_3 support could be excluded.

On the other hand, X-ray diffraction measurements on the catalyst before and after microwave heating demonstrated some important differences compared with the parallel experiments done under thermal conditions for the decomposition of H_2S. It was found that some of the alumina underwent a phase change from γ-alumina to α-alumina—a transition that only occurs at temperatures above 1273 K. It is noteworthy that, however, the maximum average temperature recorded in the microwave experiments was 1073 K. This confirmed the difference between the reaction temperature and the measured temperature. It was also observed that a considerable number of spheres as large as 2 mm containing both Al_2O_3 and MoS_2 were formed during the reaction under microwave conditions. This is further evidence for the formation of hot spots involving both the MoS_2 and the Al_2O_3 support.

These hot spots probably have temperatures 100–150 K above that of the remainder of the bulk [26], and result not only in rate enhancements, but also in apparent shifts in the equilibrium constant. The hot spots also induce a considerable reorganization of the catalyst under microwave conditions, although the exact location of these hot spots in the catalyst bed is still difficult to determine.

4. Conclusions

Microwave dielectric heating has been used to study the catalytic decomposition of hydrogen sulfide and the hydrodesulfurization of thiophene in a continuous flow reaction system. It was found that, in addition to the enhancement of reaction rate, the reaction equilibrium was apparently shifted, but in different direction for the

endothermic and the exothermic reactions. These results were attributed to the formation of spatial hot spots at higher temperatures than the average temperatures measured in the bulk catalyst material.

Experimental and theoretical studies on the possible location of remarkable temperature gradients showed that a considerable change in the inlet gas temperature had an insignificant effect on the reaction process under microwave heating, and the theoretically calculated temperature difference between the catalyst MoS_2 particles and their surrounding γ-Al_2O_3 support was also negligible.

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