

Apparent equilibrium shifts and hot-spot formation for catalytic reactions induced by microwave dielectric heating

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Received (in Cambridge, UK) 16th February 1999, Accepted 21st April 1999

Microwave dielectric heating of the gas phase decomposition of H_2S catalysed by metal sulfides on a $\gamma\text{-Al}_2\text{O}_3$ support results in significant apparent shifts in the equilibrium constant, which have been attributed to the development of hot-spots in the catalytic beds; X-ray diffraction and electron microscopy measurements have indicated the formation of hot-spots with dimensions of 90–1000 μm and which involve not only the active phase, but also the support.

The acceleration of heterogeneous catalytic processes under microwave dielectric heating conditions has attracted both academic and industrial interest.^{1–5} The majority of systems studied involve a catalyst which preferentially absorbs the microwaves relative to the support material and the reasons for the observed rate enhancements have been the subject of some controversy. The measurement of temperature under conditions where there are strong electric fields is problematical, but may be overcome, for example, by using optical fibre technology. Such measurements are still only capable of providing average temperatures. Both differential coupling abilities of materials and distribution of electromagnetic fields may result in localized temperature distribution in catalytic beds, but the contribution of these effects is difficult to quantify. Stuerger and Gaillard^{6,7} have given a thorough theoretical analysis which has conclusively demonstrated that specific athermal effects are implausible given the small energies associated with the microwave quanta and the classical nature of the heating phenomenon and have suggested that localized enhancements of the reaction rates may be responsible for non-isothermal and heterogeneous kinetic phenomena. The majority of the experimental studies on catalytic reactions under microwave conditions have dwelled on the kinetic aspects and noted that the rates of reaction and product distributions are more consistent with a temperature 300–400 K higher than that measured for the bulk of the catalyst bed. However, for supported metal catalysts, calculations^{8,9} have shown that the rate of heat transfer at 1 atm gas pressure is so high that the formation of hot-spots localised at the catalytically active sites are implausible. Here we report significant circumstantial evidence for the formation of hot-spots in the microwave experiments and have demonstrated for the first time that these hot-spots are not localised exclusively on the active catalyst, but also involve the support material. We have also estimated the dimensions of these hot-spots.

The catalytic conversion of H_2S into hydrogen and sulfur, which is commercially important for the coal and petrochemical industry,^{10,11} has recently been investigated in our laboratories using parallel microwave and conventional heating conditions. The experimental set-up is illustrated schematically in Fig. 1 and the reactions were performed under continuous flow conditions using quartz reactors. The temperature in the microwave cavity was monitored using an Accufibre optical fibre thermometer (Model 10 Luxtron) which had its tip at the centre of the catalyst sample, as shown. The microwaves were generated at 2.45 GHz using an Electro-Medical Supplies Ltd generator (0–200 W) and relayed by means of a co-axial cable to a tunable cylindrical microwave cavity placed around the reactor. The catalysts used for the study were either an

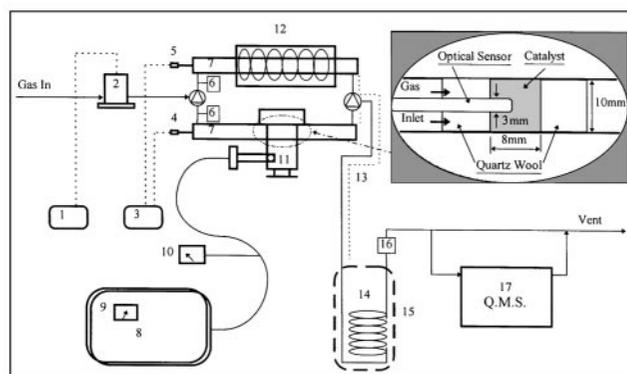


Fig. 1 Flow system for the H_2S decomposition. 1, Mass flow control unit; 2, mass flow controller; 3, temperature display; 4, optical sensor; 5, thermal couple; 6, pressure gauges; 7, quartz reactors; 8, microwave generator; 9, forward power meter; 10, reflected power meter; 11, microwave cavity; 12, conventional furnace; 13, heating tapes; 14, cold trap; 15, ice-water Dewar; 16, filter; 17, quadrupole mass spectrometer (QMS).

impregnated catalyst based on molybdenum oxide on a γ -alumina support, which was sulfided by a pre-treatment using an H_2S – H_2 flow at atmospheric pressure for 2 h, or a mechanically mixed sample of MoS_2 and γ -alumina. The reaction products were analyzed using a quadrupole mass spectrometer (QMS-200D, European Spectrometry System).

Fig. 2 compares the conversion efficiency for the decomposition of H_2S under microwave and conventional thermal conditions in the temperature range 500–1100 K for both the impregnated catalyst and the mechanical mixture of MoS_2 and γ -alumina (both 30% by weight MoS_2 on γ -alumina). Fig. 2 also illustrates the calculated equilibrium conversion efficiencies based on thermodynamic data of Kaliotas and Papayannakas.¹² It is noteworthy that for such an endothermic reaction the conversion efficiencies are relatively low and that for the conventional thermal reaction the experimental observed per-

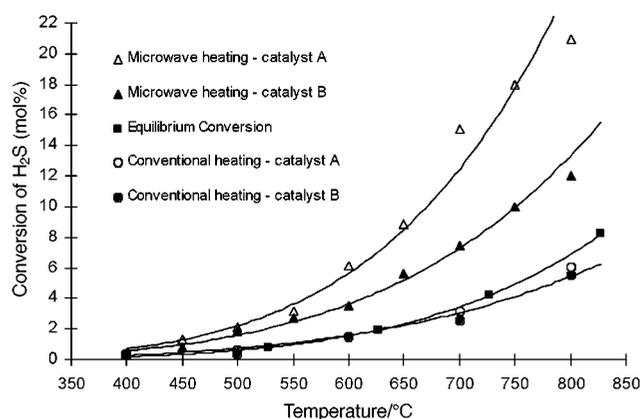
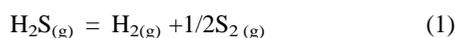


Fig. 2 H_2S conversion vs. temperature with mechanically mixed catalyst A and impregnated catalyst B

Table 1 Dielectric properties of the chemicals (25 °C, 2.45 GHz)

Chemical(s)	Dielectric constant, ϵ'	Dielectric loss, ϵ''	Dielectric loss tangent, $\tan \delta$
γ -Al ₂ O ₃	2.678	0.01768	0.006604
MoS ₂ / γ -Al ₂ O ₃ (impregnated)	2.971	0.2694	0.09068
MoS ₂ + γ -Al ₂ O ₃ (mechanically mixed)	3.115	0.3162	0.1015
MoS ₂	3.331	0.6410	0.1924

centage conversions are in good agreement with the equilibrium data. The basic reaction is given by eqn (1)



with negligible production of other gaseous sulfur species.¹² Surprisingly, the conversion efficiency for the reaction which takes place in the microwave cavity is higher than that predicted on thermodynamic grounds. For the impregnated catalyst the percentage conversion at a temperature of 800 °C has risen from *ca.* 6.5% with conventional heating to 12% when microwaves are used. The effect is even greater for the mechanically produced catalyst, where the conversion efficiency has risen to 21% under microwave heating at 800 °C. We have concluded that these observations are not due to any athermal microwave effect, but rather that the selective features of microwave dielectric heating have induced an anisotropic temperature profile on the catalytic bed which is giving rise to 'apparent' shifts in the equilibrium constant for the reaction.

The dielectric measurements on MoS₂, the impregnated catalyst and the support materials, which are summarised in Table 1, clearly indicate that the catalysts are more 'lossy'¹³ than the support materials and will initially preferentially absorb the microwave energy. The extent to which the heat is then transferred to the support has not previously been addressed. While the dielectric loss of γ -alumina is temperature dependent, particularly in the high temperature range, this temperature rise may be amplified to develop hot-spots. Such hot-spots could not only give rise to increased reaction rates, but also, if the residence times of the gases flowing over the catalyst are relatively long compared to the half-lives for the reaction, then they could create local shifts in equilibrium constant. To our knowledge attention has not been drawn previously to large equilibrium shift effects arising from this phenomenon.

We have argued that these 'apparent' equilibrium shift effects may be enhanced if the catalyst had a higher concentration of hot-spots, or had a higher temperature of hot-spots. Although, the maximum rate enhancements are achieved using a well dispersed catalyst with a high surface area, the hot-spot phenomenon is accentuated by having a poorly dispersed catalyst, such as that produced by mechanically mixing MoS₂ and γ -alumina.

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. By using this principle the hot-spot temperatures given in the second and third columns of Table 2 were calculated. The hot-spot temperatures for the impregnated and

Table 2 Hot-spot temperatures calculated for impregnated catalyst and mechanical mixture of MoS₂ and γ -Al₂O₃

Probe temp./°C	Hot-spot temp./°C impregnated catalyst	Hot-spot temp./°C mechanically mixed catalyst
500	600	650
600	700	770
700	810	890
800	920	1010

mechanically mixed catalysts are respectively *ca.* 100 and 200 °C higher than the temperature measured by the probe.

X-Ray diffraction measurements on the catalyst before and after microwave heating have demonstrated some important differences compared with the parallel experiments done under thermal conditions. Firstly, some of the alumina undergoes a phase change from γ - to α -alumina—a transition which only occurs at temperatures above 1273 K.¹⁴ It is noteworthy that the maximum average temperature recorded in the microwave experiments was 1073 K. The average crystallite size calculated from the peak widths of five intense peaks is 90 μm . Secondly, the molybdenum disulfide, which was initially evenly distributed as 150–170 μm amorphous particles (electron microscopy measurements), forms some hexagonal crystals during the microwave process. Since the melting point of MoS₂ is 1458 K, this is further evidence for the formation of hot-spots involving both the MoS₂ and the alumina support. The electron microscopy studies have also indicated that considerable migration of MoS₂ has occurred during the reaction since spheres as large as 1000 μm containing both Al₂O₃ and MoS₂ are formed. Surface area and size pore measurements have also confirmed that a considerable reorganisation has occurred and has resulted in a decrease in the surface area.

In summary, the preferential heating effects associated with microwave dielectric heating can give rise to hot-spots which result not only in rate enhancements, but also in apparent shifts in the equilibrium constant. These hot-spots probably are larger than 90 μm and may be as large as 1000 μm and have temperatures 100–200 K above that of the remainder of the bulk. The hot-spots also induce a considerable re-organisation of the catalyst under microwave conditions.

The selective nature of the dielectric heating effect cannot be reproduced easily using conventional heating methods. This phenomenon is not only interesting from an academic perspective because the results are initially counter-intuitive, but since it has the potential to increase the conversion efficiencies of reactions with low yields by an order of magnitude, whilst maintaining the same operating temperature as a conventionally heated reactor, it is not without commercial potential.

BP is thanked for endowing DMPM's Chair and EPSRC are thanked for financial support.

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