

https://dspace.org/

The effect of microwave treatment on potassium promoted iron Fischer-Tropsch catalysts

Dlamini, Mbongiseni William

2012-07-03
http://hdl.handle.net/10539/11587

Downloaded from a DSpace repository. https://dspace.org/

Chapter 1

Microwave chemistry

1.1 Microwave heating

1.1.1 Introduction

While fire is now rarely used in synthetic chemistry, it was not until Robert Bunsen invented the "Bunsen" burner in 1855 that the energy from this heat source could be applied to a reaction vessel in a focused manner. The Bunsen burner was later superseded by the isomantle, oil bath or hot plate as a source of applying heat to a chemical reaction. In the past decade, heating chemical reactions by microwave energy has moved the heating methodology into yet another direction. It has become an increasingly popular heating method used by the scientific community.[1] Microwave heating provides an alternative method to convectional conductive heating for introducing energy into catalytic reactions.

Advances towards the development of microwave technology were started during the Second World War when a magnetron was designed by Randall and Booth at the University of Birmingham in England. Magnetrons were designed to generate fixed frequency microwaves for RADAR (Radio Detection And Ranging) which could be used for detecting enemy planes during the war. By 1941, 17 magnetrons for radar systems were being produced per day at Raytheon. It was in this period that Percy Lebaron Spencer of the Raytheon Company accidentally discovered that microwave energy could cook food when he noticed that a chocolate bar in his pocket had melted while he was standing in front of an open magnetron. After performing several "tests" including popping popcorn and exploding eggs he concluded that microwaves could increase the internal temperature of foods much quicker than a conventional oven; thus the microwave oven was invented.

The electromagnetic spectrum is a continuum of all electromagnetic waves arranged according to frequency and wavelength. Microwaves are part of this electromagnetic

spectrum, occupying the region between infra-red and radio frequencies which corresponds to wavelengths of 1 cm to 1 m (frequencies of 30 GHz to 300 MHz). The wavelengths between 1 cm and 25 cm are mainly used for RADAR transmissions and the remaining wavelength range is used for telecommunications. Industrial and domestic appliances are only authorized to operate at 915 MHz or 2.45 GHz (wavelength 32.8 or 12.2 cm, respectively) to avoid interfering with radar or telecommunication frequencies.[2] Within this region of electromagnetic energy, only molecular rotations of molecules are affected by the radiation.

Microwave energy consist of two components: an electric field and a magnetic field, though only the electric field transfers energy to heat a substance.[3] The electrical and magnetic components of a microwave are shown in Figure 1.1. Magnetic field interactions do not normally occur in chemical synthesis. Microwaves move at the speed of light (300, 000 km/s). The energy in microwave photons ($9.65x10^{-4}$ to $9.65x10^{-2}$ kJ/mol) is very low relative to the typical energy required to cleave molecular bonds (335 – 500 kJ/mol), thus microwaves do not affect the structure of a molecule.

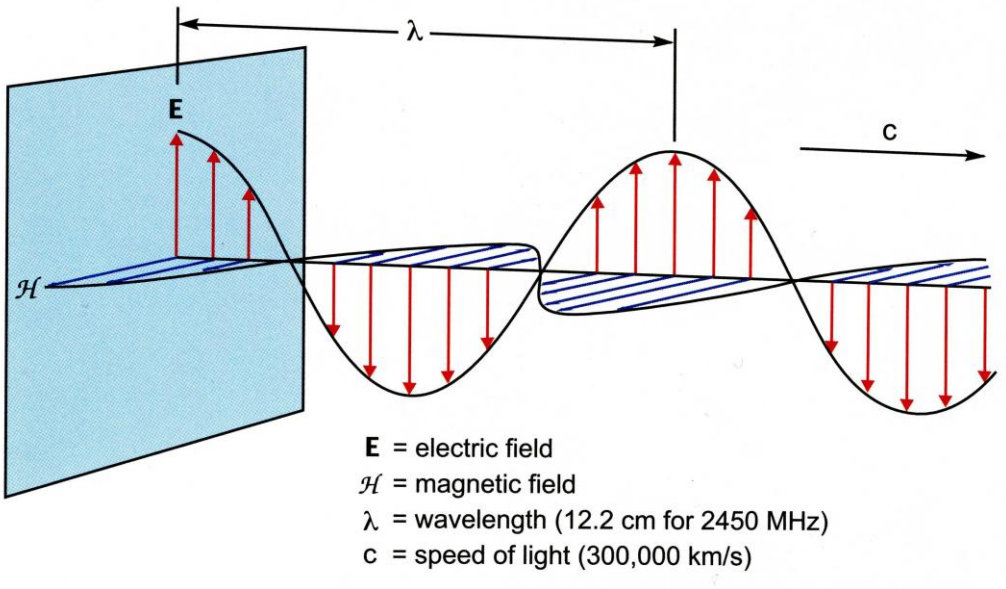


Figure 1.1 The electric and magnetic components of microwaves.[4]

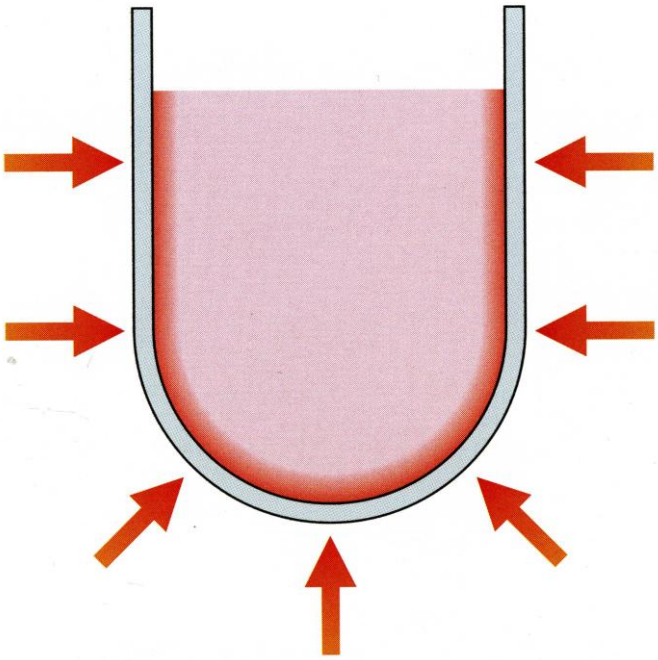
1.1.2 Properties of microwave heating

Although microwaves are best known for their use in domestic microwave ovens, they are used in a wide array of heating applications; from industrial-scale processing,[5] through medical use,[6] to synthesis in the research laboratory.[7] This is due to some fundamental differences in the way in which a material is heated by microwaves when compared to conventional methods,[8] and the high efficiency that can result from heating only the target rather than maintaining an oven or vessel at an elevated temperature.

A distinguishing feature of microwave heating is its volumetric nature whereby the microwave power is dissipated in a dielectric and the electromagnetic energy is converted directly to heat inside the sample. Regions of localized superheating are thus observed under microwave heating. This is in contrast to conventional heating where heat enters the sample through its surface and is transferred towards the centre of the sample mainly by thermal conduction.[9] A comparison of the two types of heating is shown in Figure 1.2. From this diagram it can be seen that in a conventionally heated sample the inside temperature is usually lower than the surface temperature due to conduction. This inefficient mode of energy transfer results in undesirable temperature gradients within the sample.

The *in situ* mode of energy conversion seen in microwave heating has many advantages for chemists because its magnitude is directly related to the properties of the molecules being heated. This means that microwaves can be used for selective heating of materials, and this phenomena finds many applications in chemistry. For example, microwaves can initiate a chemical reaction that is not possible by conventional heating. Because microwaves can penetrate materials and deposit energy in them, there is generation of heat throughout the volume of the material. It is therefore possible to achieve rapid and uniform heating.

(a)



(b)

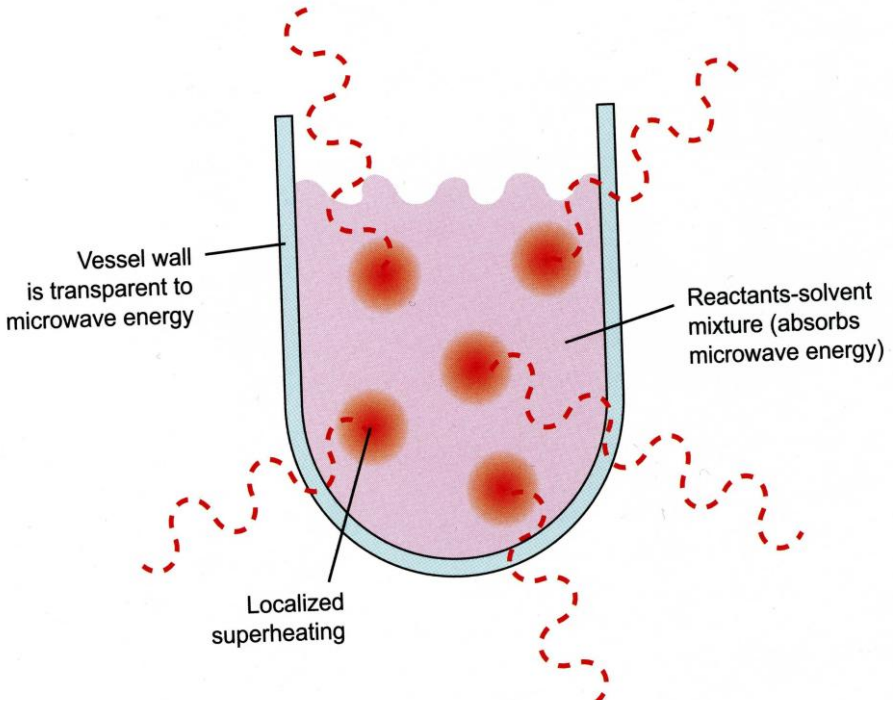


Figure 1.2 Schematics of sample heating by (a) conduction and (b) microwaves.[4]

1.1.3 Fundamentals of microwave heating

Based on a material's response to microwaves, materials can be broadly classified as follows: (i) materials that are transparent to microwaves, e.g. sulfur, (ii) materials that reflect microwaves, e.g. copper, and (iii) materials that absorb microwaves, e.g. water.[10] It is the materials that absorb microwaves that are critical in microwave chemistry. The principle of microwave heating is that the oscillating electrical field of microwaves interacts directly with the molecular dipoles and/or charged ions present in the sample being heated. Microwave irradiation triggers heating by three main mechanisms – dipolar polarisation, ionic conduction and interfacial polarization. While the dipolar polarization mechanism (also called dielectric heating) explains the heating phenomena of dipoles, the ionic conduction mechanism explains the heating in samples with free ions or ionic species. The interfacial polarization (also called the Maxwell-Wagner effect) mechanism describes the heating in non-homogeneous systems created by the suspension of conducting particles in a non-conducting medium.

1.1.3.1 Dipolar polarization

If a dipole is exposed to an electric field, it normally aligns itself with the field to minimise the free energy. The time taken for this alignment (known as the response time) is dependant on the frequency of the field and the strength of the dipole. Considering the frequency dependency of the response time, three scenarios are possible. At low frequencies the time taken by the electric field to change direction is larger than the response time for the dipoles, hence the dipoles remain aligned with the electric field. At high frequencies the electric field changes direction much faster than the response time of the dipoles, hence the dipoles are unable to rotate and they remain static. However, in the microwave range of frequencies the time required by the field to change direction is of the same magnitude as the response time of the dipoles. The dipoles experience torques that causes them to rotate as they try to orient themselves with the field, but the resulting polarization of the molecule lags behind the changes of the field. As the dipoles are not perfectly aligned with the field, they are not in the lowest energy state, hence an energy transfer must be occurring. The lag indicates that the molecule absorbs energy from the electromagnetic field and is being heated.[11]

Many factors define the dielectric properties of materials including the dielectric constant, the dipole moment, the dielectric loss and the dielectric loss tangent. The dielectric constant (ε') also known as the relative permittivity describes the ability of a molecule to be polarized by an electric field, it is dependant on both temperature and frequency. This value reaches a maximum at low frequencies since this is when a maximum amount of energy can be stored in a material.

A dipole moment, μ, (measured in Debye units, D) is a product of the distance between the centres of charge in a molecule (r) multiplied by the magnitude of that charge (Q). In general, molecules with large dipole moments also have large dielectric constants.

$$\mu = Qr \tag{1.1}$$

The dielectric loss (ε'') is used to measure the efficiency with which energy of the electromagnetic radiation is converted into heat. It is this value that provides chemists with the coupling efficiency of a particular solvent. The ratio of the dielectric loss and the dielectric constant defines another parameter called the dielectric loss tangent (tan δ), which defines the ability of a material to convert electromagnetic energy into heat energy at a given temperature and frequency:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{1.2}$$

where ε' is the dielectric constant and it describes the ability of a molecule to be polarized by an electric field. From this equation it can be seen that under the same microwave heating conditions some materials are more capable than others of absorbing microwave radiation energy because of their higher dielectric loss tangent property. Table 1.1 shows loss tangents for common solvents.

Table 1.1 Loss tangents (tan δ) of selected solvents (2.45 GHz, 20°C).[12,13]

Solvent	tan δ	Solvent	tan δ
Ethylene glycol	1.350	1,2-Dichloroethane	0.127
Ethanol	0.941	Water	0.123
DMSO	0.825	Chloroform	0.091
Methanol	0.659	Acetonitrile	0.062
1,2-Dichlorobenzene	0.280	Tetrahydrofuran	0.047
NMP	0.275	Dichloromethane	0.042
Acetic acid	0.174	Toluene	0.040
DMF	0.161	Hexane	0.020

1.1.3.2 Ionic conduction

This mechanism of energy transfer from microwaves to a sample requires the presence of ions or ionic species in the sample. The electric field of the microwaves generates ionic motion as the ions try to realign themselves to the rapidly changing field, resulting in rapid superheating. Ionic conduction is sensitive to temperature; as the temperature increases, the transfer of energy becomes more efficient. Alumina, for example, has a conductivity that rises with temperature, as the number of electrons thermally excited into the conduction band increases. This can lead to the phenomenon known as thermal runaway.[11]

The ionic conduction mechanism provides scientists with a useful tool, especially when studying the behaviour of ionic liquids (IL) under microwaves. Ionic liquids are a special type of solvent that are made up of ions. These solvents are distinct because of their negligible vapour pressures, they are miscible with most non-polar solvents, they have a wide accessible temperature range (>300 °C) and they have low toxicity. Because they are highly polar, ILs can be heated at heating rates above 10 $^{o}Cs^{-1}$ without any significant build-up of pressure.[14] It is important to note that the ionic conduction mechanism represents a much stronger effect than the dipolar polarization mechanism with respect to the heat-generating capacity, and this has great consequences for the synthesis of nanoparticles in ionic liquids.[1]

1.1.3.3 Interfacial polarization

The interfacial polarisation method can be considered as a combination of the conduction and dipolar polarisation mechanisms. It is important for heating systems that comprise of a conducting material dispersed in a non-conducting material. For example, consider the dispersion of metal particles in sulphur. Sulphur does not respond to microwaves, and metals reflect most of the microwave energy they are exposed to, but combining the two makes them a good microwave-absorbing material. However, for this to take place, metals have to be used in powder form. This is because, unlike a metal surface, metal powder is a good absorber of microwave radiation. It absorbs radiation and is heated by a mechanism that is similar to dipolar polarisation. The environment of the metal powder acts as a solvent for polar molecules and restricts the motion of ions by forces that are equivalent to inter-particle interactions in polar solvents. These restricting forces, under the effect of an oscillating field, induce a phase lag in the motion of ions. The phase lag generates a random motion of ions and results in the heating of the system.[15]

1.1.4 Microwave irradiation methods

While early breakthroughs in microwave-assisted synthesis were done in domestic microwave ovens, laboratory microwave ovens have increased in sophistication and utility to include models specific for use in the chemical and biological sciences. Experimental parameters like the irradiation power level, reaction temperature and pressure inside the reaction vessel are not known precisely in a domestic microwave oven. These uncertainties represent a serious safety issue and also lead to a lack of reproducibility[16]. However, more technical systems now offer built-in magnetic stirrers, direct temperature and pressure monitoring by utilising various probes and sensors. Microwave devices can be classified into two categories depending on the method used to irradiate samples; single-mode or multi-mode devices.

1.1.4.1 Single-mode microwave devices

In this mode the reactor is inserted directly into the waveguide of the microwave. A waveguide is a rectangular channel with reflective walls, which enables the transmission of

microwaves from the magnetron to the microwave cavity or applicator. The waveguide is designed in a manner that promotes an in phase reflection of microwaves, provided the waveguide is empty. This results in a standing wave pattern, which is an interference of fields that have the same amplitude but different oscillating directions (Figure 1.3). Samples are only placed at the antinodes of the standing wave since this is where the intensity of the microwave radiation is the highest. Unfortunately this requirement tends to limit the number of vessels that can be irradiated to only one at a time.

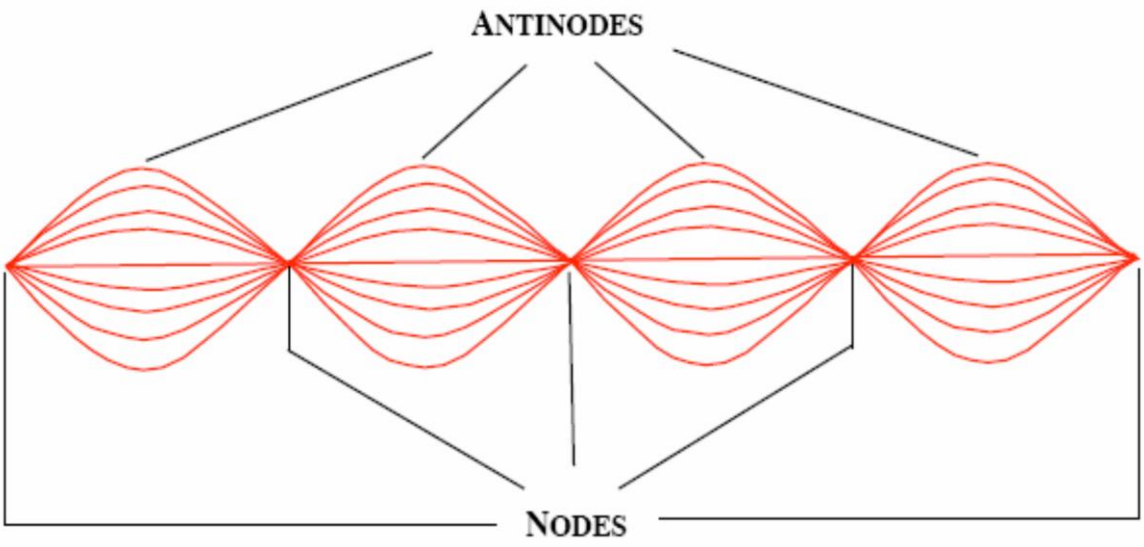


Figure 1.3 Generation of a standing wave pattern.[15]

Because single-mode devices are based on solutions of Maxwell equations, areas of high and low magnetic field strength are known.[17] Even though the electromagnetic field distribution is non-uniform in these devices, it is nonetheless predictable and hence it can be focused in a particular location. Palaith and Silberglitt[18] have utilized the ability of mono-mode applicators to focus microwaves when joining ceramics. The ability to focus microwaves proved to be key in their work because only the joint interface had to be heated with the microwaves and not the entire ceramic. Other interesting features of this mode of device includes; an adjustable electric field strength, a well-known field distribution, precise control of the energy input, the possibility to determine dielectric properties of substances; they also have the highest heating rates. One of the limitations of the single-mode apparatus is that the effective sample space is very limited (often to only a few millimetres) because the microwave cavity is part of the waveguide.[19] Even though single-mode devices work well at

laboratory scale, it is difficult to scale them up for industrial applications due to geometry limitations and non-uniformity of the fields.

1.1.4.2 Multi-mode microwave devices

The simplest and cheapest example of these types of devices is a domestic microwave oven. In this type of device, the aim is to create new modes (wave kinds) by using refraction, reflection and interference. The wave chaos created avoids the occurrence of standing waves, which results in a system with high power density (radiation intensity). Unlike in single-mode devices where the microwave cavity is part of the waveguide, in multi-mode systems the radiation produced by the magnetron is directed through a waveguide and a mechanical field distributor into a reasonably large microwave cavity. The microwaves that enter the cavity are reflected either by the walls of the microwave oven or the sample to create new wave kinds. In many multi-mode devices, a mode stirrer is then used to ensure uniformity of the microwave field.[1] Mode stirrers are reflectors that are irregularly shaped; they rotate within the cavity and redistribute the electromagnetic field. Turntables that rotate during operation are also used to improve the uniformity of the field. Both mode stirrers and turntables create time-averaged uniformity. Although multi-mode systems do not focus microwave energy as effectively as their mono-mode counterparts, they have been used successfully to process multiple samples and have found specific application in large-scale preparations of materials.[3]

1.1.5 Temperature measurement in a microwave field

The measurement of temperature in the microwave field is a complex exercise. Typical thermometers cannot be used for temperature measurement in the microwave field because they contain mercury or an alcohol, both of which couple with microwaves. When typical thermometers are exposed to a microwave field, the result is not only a measure of the sample temperature, but also that of the heating effect of the mercury or alcohol as they interact with the microwaves. However, this effect has been shown to be minimal when the expansive liquid used has a low dielectric loss tangent such as xylene.[8] Conventional metal-based

thermocouples cannot be used because they absorb microwave energy and heat up under spark formation.[19]

Early work on microwave-assisted reactions ignored temperature measurement because of its complexity.[20-22] Presently, there are three main methods that are used to measure temperature;

i) Shielded thermocouples
ii) Infrared sensors
iii) Fibre optic sensors

1.1.5.1 Shielded thermocouples

Conventional thermocouples measure temperature by converting thermal energy into a change in electrical resistance at a junction between two different metals. For economic reasons, it is attractive to use conventional thermocouples to measure temperature in a microwave field. However, if a standard thermocouple is exposed to a microwave field it tends to concentrate the electrical charges which in turn perturbs the microwave field. Heating or arcing effects may be induced at the thermocouple junction as a consequence of the concentrated electrical fields, and the thermocouple device can also become non-functional. The concentration of electrical charges in a thermocouple increases for sharper probe tips and thermocouple jackets with smaller diameters. This phenomenon and others explain why standard thermocouples may record higher temperatures than expected when exposed to a microwave field. Shielded thermocouples are a modification of standard thermocouples and are used to overcome these effects.

In a shielded thermocouple, a standard thermocouple is housed in an electrically conductive tube that is thermally stable. Typically the thermocouple is further enclosed in a microwave transparent ceramic sheath to ensure that the thermocouple is well protected. Shielding protects the thermocouple from the microwave field by covering the thermocouple junction and also by increasing the diameter of the thermocouple that is exposed to the microwave field.[23] Shielded thermocouples are the least expensive option available for temperature measurements in a microwave field. The accuracy of these devices is low when studying non-

polar solvents like dichloromethane since they then act as antennas, and get heated upon exposure to microwave radiation.

1.1.5.2 Infrared sensors

Infrared (IR) sensors are a "non-contact" type of temperature measuring devices. They are based on the physical principle that every solid body emits radiation when hot. The emitted radiation is directly proportional to the emission coefficient and the fourth power of the absolute temperature (also known as the thermodynamic temperature) of the hot body. The relationship describing this phenomena is given by the Stefan-Boltzmann law:

$$J^* = \varepsilon \alpha T^4 \qquad (1.3)$$

where J^* is the energy flux density, ε is the emission coefficient of that particular body, α is the Stefan-Boltzmann constant and T is the absolute temperature. Since most bodies also absorb infrared radiation, IR sensors are only placed on the reaction vessel's wall. This indirect method for temperature measurement has been widely used in the literature.[24-26] The sensors are integrated into the walls of the microwave cavity and they detect the surface temperature of the reaction vessel from a pre-defined distance. It is assumed that the measured temperature on the outside of the reaction vessel will correspond more or less to the temperature of the reaction mixture contained inside the reaction vessel. This, however, is the biggest disadvantage of this method, because the measured temperature may not accurately represent the bulk temperature inside the reaction vessel due to cooling effects. Also, in microwave heating the reactor walls are the coldest regions in the system because of the inverted heat flux in comparison to conventional heating. Therefore, the reaction mixture is always warmer than the reactor wall.

Compared to shielded thermocouples and fibre optic probes, IR sensors always record lower temperatures than its counterparts because it is an indirect method (Figure 1.4). An error of ΔT = 30 K is associated with this method, especially when reaction mixtures are heated quickly and when reaction times are short.[27] Key advantages of this method of measurement are its low cost and its wide measuring range of -40 ^{o}C to +1000 ^{o}C.

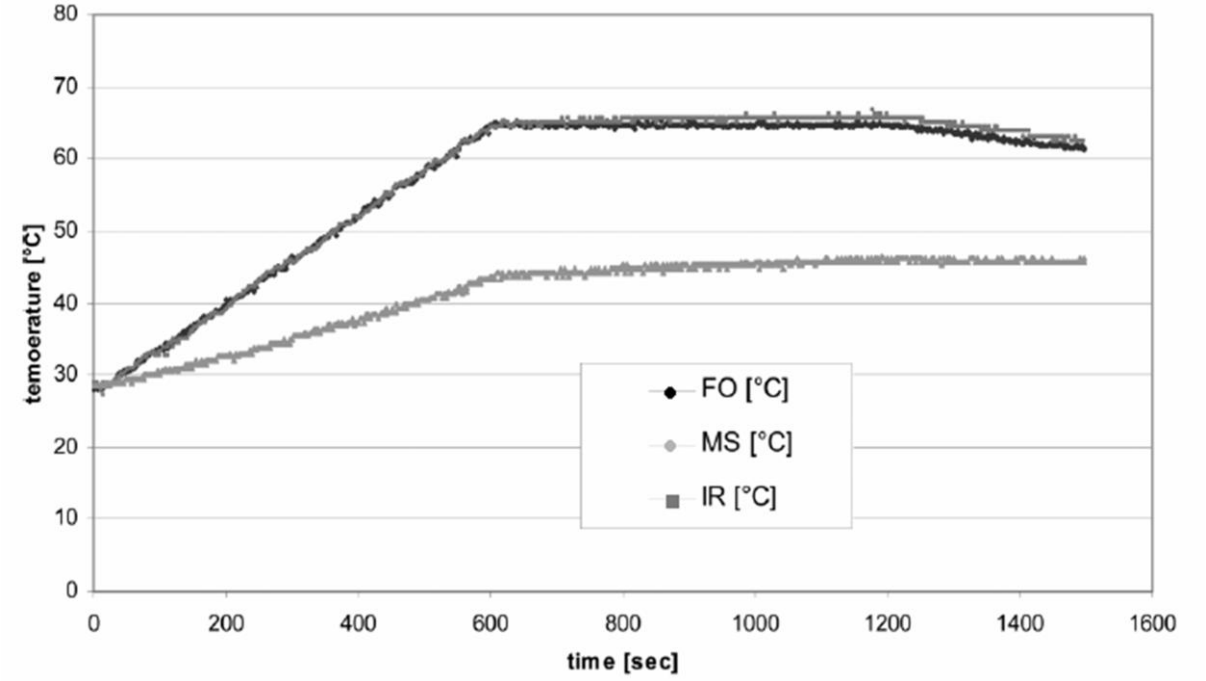


Figure 1.4 Comparison of temperature measurement with different sensors in the temperature range: 28 ^{o}C to 65 ^{o}C. The fibre optic sensor (FO) and the metal sensor (MS) [shielded thermocouple] are placed directly into the stirred medium and their precision is ± 2 K. The IR sensor measures the temperature on the outer surface of the reactor.[27]

1.1.5.3 Fibre optic sensors

A more accurate way of monitoring temperature in a microwave chemistry experiment is to directly determine the temperature of the reaction mixture by utilizing an internal fibre-optic (FO) sensor.[28,29] These sensors are placed directly into the reaction mixture hence their output reflects the actual temperature of that particular reaction mixture. FO sensors operate on the basis of currents induced by the field in a small amount of a slightly conductive material, which in turn produces Joule heating. In a typical sensor, a gallium arsenide crystal is used as the conductive material and it is glued onto the tip of the sensor using a polymer. Compared to shielded thermocouples and IR sensors, FO probes are more accurate and faster responding but they are expensive.

Challenges associated with this method originate from the use of the fragile sensor crystal. Because a polymer is used to glue the crystal to the sensor tip during fabrication, it is not

possible to use these probes at low temperatures. This limitation narrows the operating range of FO sensors to temperatures ranging from 0 to 330 ^{o}C, although a precision of $\Delta T = 2$ K can be achieved. Permanent ageing phenomena of the sensors are already observed above 250 ^{o}C after a few hours.[27] Another disadvantage of this method is the high sensitivity of the crystal sensor towards mechanical stress. Consequently, the probe is usually protected by the use of protective immersion wells. This increases the lifetime of the probe but slows down the response time.[29] In an effort to increase accuracy, Obermayer and Kappe[30] have suggested that the simultaneous measurement of temperature using both external IR and internal FO sensors in a microwave chemistry experiment can have significant advantages compared to relying on the output of only one of these sensors. Indeed from their findings, important information about the dielectric properties and exothermicity of a chemical reaction performed under microwave conditions was obtained.

One way of understanding the differences observed between microwave and conventionally heated reactions, is to analyse the temperature dependence of reactions. Chemical reactions are classified into two categories; kinetic and thermodynamic reactions. Kinetically controlled reactions typically require mild conditions to reach completion, because upon attaining the resonance-stabilized intermediate, the path with the least activation energy is normally taken. Chemical reactions driven by conventional heating are more likely to occur under kinetic control.[4] On the other hand, microwave-assisted reactions are more likely to occur under thermodynamical constraints. This is due to the fact that thermodynamically controlled reactions require harsh conditions to reach completion, since they have higher activation energies. It is also known that a small activation energy generally corresponds to a rate constant that does not increase rapidly with temperature, whereas a reaction which is strongly dependent on temperature will have a large activation energy. Since the rapid molecular-heating present during microwave heating results in the attainment of very high temperatures, it can be expected that microwave driven reactions will be thermodynamically controlled since these have high activation energies. This may explain the origin of the differences in products and reaction rates obtained when either microwave driven and conventionally heated reactions are studied.

1.2 Microwave-enhanced chemistry

In an ideal world, chemical transformations occur at room temperature, reach full conversion within a few minutes, and provide quantitative isolated product yields. The reality, however, is quite different. Many synthetically relevant processes necessitate an elevated temperature regime in order to proceed, with reaction times of several hours or even days to drive a reaction to completion being the norm.[31] However, the application of microwave technology in synthetic chemistry has been an invaluable innovation. The efficiency of microwave flash-heating offers numerous advantages over classical methods of introducing heat into chemical reactions. These advantages include: reduced reaction times, faster energy absorption, reduced thermal gradients and selective heating amongst others. Microwave-assisted chemistry has blossomed into a mature and useful technique since its discovery in 1986,[21,22] although initial reports indicated that the potential of this technique had been published in 1981 for chemical synthesis[32] and in 1967 for polymer applications.[33]

1.2.1 Microwave-assisted organic synthesis

When heating is done conventionally, the refluxing conditions in organic synthesis are generally controlled by the boiling point of the solvent. That is, solvents with high boiling points are used for reactions that occur at high reaction temperatures. In contrast, microwave heating causes superheating of the solvent and hence the boiling point of a solvent is less significant in controlling reaction temperatures. Baghurst and Mingos[34] have shown that polar liquids can be overheated by 13−26 ^{o}C above their normal boiling points under microwave heating. This phenomenon can be explained by an "inverted heat transfer" mechanism that occurs in MW heating (from the irradiated medium towards the exterior) since boiling nuclei are formed at the surface of the liquid. This effect has been used to explain the enhancement in reaction rates observed in organic and organometallic chemistry.[35] Time is an important factor in organic synthesis especially when a library of compounds is being made using a trial-an-error procedure in the synthesis of new compounds. Microwave-assisted organic synthesis (MAOS) is now an accepted method for dramatically reducing reaction times.[36,37]

MAOS has been applied in various reactions including Suzuki coupling,[38-40] Hoffmann elimination,[41-43] Diels-Alder reactions,[44] Mannich reactions[45] and Michael addition reactions.[46] The application of microwave heating in these systems gives higher yields, higher selectivities (minimized formation of undesired by-products) and also reduces the reaction time from hours to just a couple of minutes. An example is the exploitation of the different dielectric properties of water and chloroform in the Hofmann elimination reaction reported by Strauss and Trainor.[41] The aim of their study was to produce aryl vinyl ketones from the corresponding quaternary ammonium salts (see Figure 1.5) using a Hofmann elimination mechanism. Problems are encountered if this reaction is performed using conventional heating since the conjugated ketones produced are heat-sensitive and polymerization is difficult to avoid at high temperatures. These researchers performed the reaction successfully by stirring a mixture of N-[2-(4'-ethoxybenzoyl)ethy]-N, N, N-trimetylammonium iodide, water and chloroform under microwave heating. They reported a product yield of 96%. Typically, 40 seconds after commencement of the reaction, the temperatures of the aqueous and the organic phases were 105 and 48 °C respectively, due to differences in the dielectric properties of the solvents. As the reaction proceeded the product, 4'-ethoxyphenyl vinyl ketone, was extracted and diluted into the poorly microwave-absorbing, cooler, organic phase hence avoiding the secondary polymerization reaction.

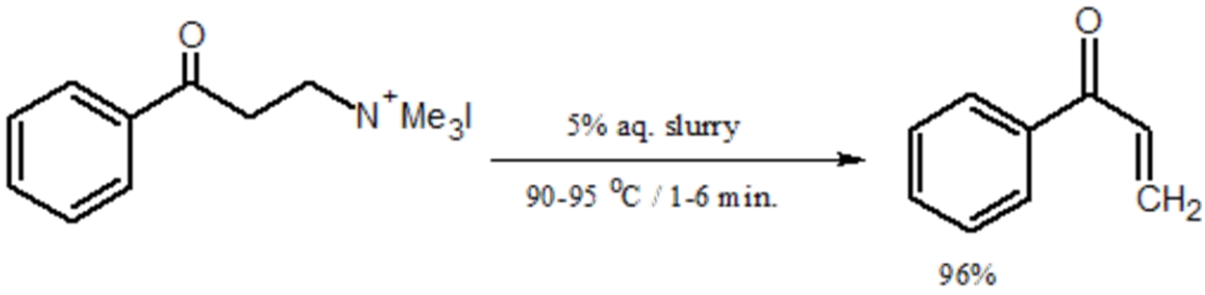


Figure 1.5 A scheme showing the production of aryl vinyl ketones from a corresponding quaternary ammonium salt.

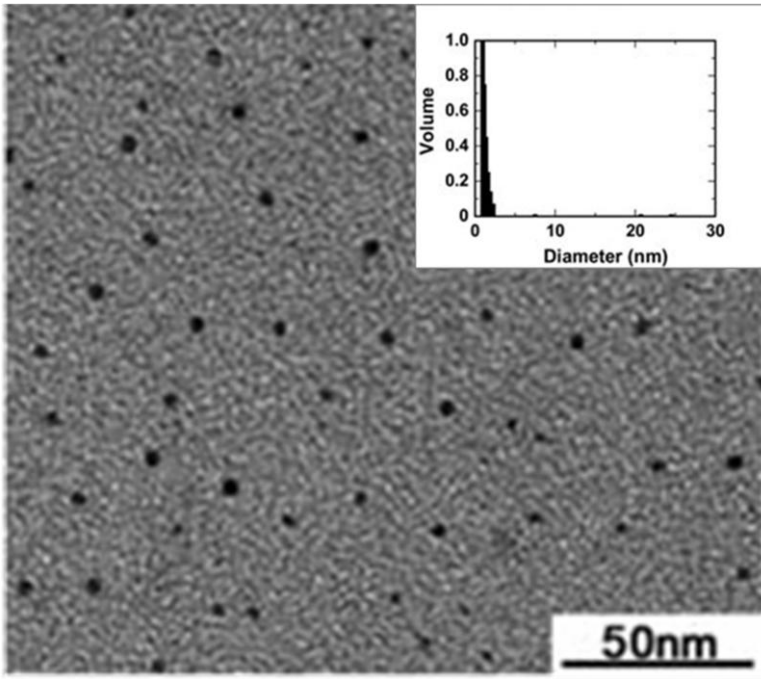
1.2.2 Microwaves in nanomaterials chemistry

Nanomaterials continue to attract a lot of research interest because they mark a material transition range between molecular and bulk properties. It is well known that upon decreasing the crystallite size of any material, bulk properties are lost as the fraction of surface atoms

becomes large.[47,48] Nanoparticles are in the particle size range of 1−100 nm and they tend to exhibit novel and significantly changed physical, chemical and biological properties due to their size. Tremendous efforts are being made towards controlling the particle size, particle size distribution, shape, dispersion and structure of nanomaterials using the effective heating provided by microwave irradiation. Horikoshi and co-workers[49] have shown that MW heating leads to a 5.7-fold enhancement of the heating rate relative to oil-bath heating when synthesizing silver nanoparticles. This was after they observed that heating an aqueous solution of carboxymethylcellulose/diaminesilver(I) solution at continuous 64 Watt microwave irradiation gave a 0.51 $^{o}Cs^{-1}$ heating rate, whereas for the oil-bath heating method a rate of 0.09 $^{o}Cs^{-1}$ was obtained at a power consumption of 400 Watts. Consequently, smaller particles with a fairly narrow particle size distribution (1.8 to 3.6 nm; average size ~3 nm) were achieved under microwave heating, while conventional heating produced a broader particle size distribution of 1 to 5 nm (Figure 1.6).

Another recent application of microwave heating is in the purification of carbon nanotubes (CNTs), with several researchers reporting improved results of purification by microwave assisted acid digestion. It has been shown theoretically and experimentally that a 'perfect' CNT is a ballistic conductor, that is, its resistance is quantised and is thus independent of length due to its unique 1D structure.[50,51] Therefore microwave energy is not transferred into the CNT structure but to any impurities that may be present, for example, the metal particles from which CNTs are grown. As the catalysts metal particles are exposed to MW radiation, localised heating is observed thus promoting their removal from the CNT. In contrast, laboratory prepared CNTs have structural imperfections. Thus joule heating occurs leading to superheating of the CNTs. This is potentially of benefit as the defective and damaged CNTs may be supplied with sufficient energy to re-orient any 'imperfect' sp^3 carbon bonds into the desired sp^2 configuration, or the defective CNTs may be thermally destroyed leading to an increase in the average CNT quality.

(a)



(b)

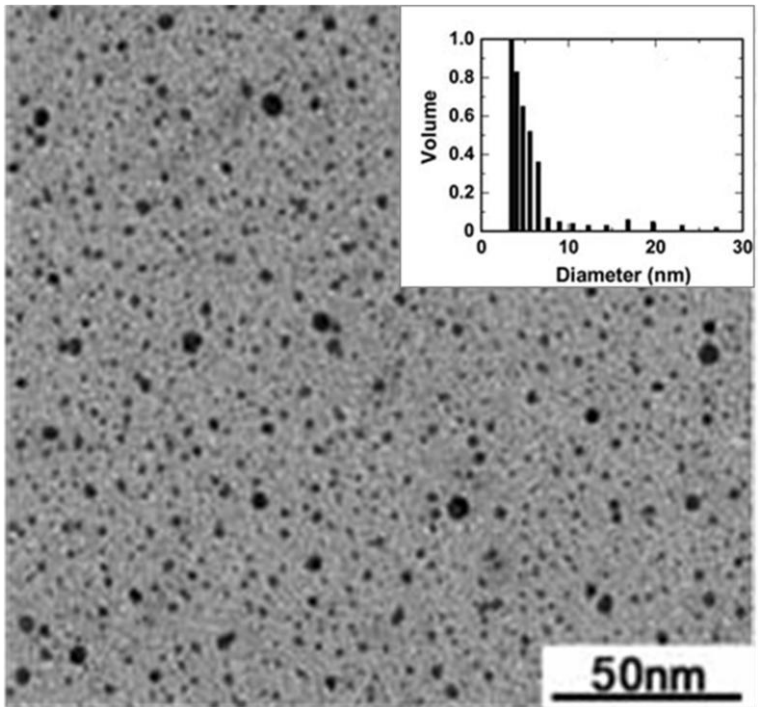


Figure 1.6 TEM images of silver nanoparticles produced using (a) microwave and (b) oil bath heating methods. Insert: The corresponding particle size distributions for the different heating methods.[49]

1.2.3 Microwaves in catalysis

By definition, a catalyst is a material that accelerates the rate of a chemical reaction without itself undergoing any net chemical change. Catalysts function by providing an alternative pathway in going from a reactant to a product with a lower Gibbs energy of activation, $\Delta^{\ddagger}G$. The alternative pathway avoids the slow, rate-determining step of the uncatalysed reaction, resulting in an enhancement of the reaction rate under the same conditions. It should be noted nonetheless that a catalyst does not affect the Gibbs energy of the overall reaction, $\Delta_r G^{\theta}$, because G is a state function. Catalysis is a purely kinetic phenomenon and it does not change the equilibrium of a reaction, but it only alters the rate at which it is attained. Therefore, reactions that are thermodynamically unfavourable cannot be made favourable by a catalyst. Research in catalysis is motivated in part by the possibility of designing nanostructured catalysts that possess novel catalytic properties such as low-temperature activity, selectivity, stability and are resistant to poisoning and degradation effects. Since the energy of MW quanta is not sufficient to achieve direct electronic excitation of reagents or the breaking of chemical bonds, MW heating is considered to be a probable way for activating solid catalysts.[52]

1.2.3.1 Oxidative coupling of methane to higher hydrocarbons

Natural gas, which is between 70 to 90% methane, is an environmentally friendly and abundant resource that has been studied extensively. Methods have been explored to provide to provide an economically viable process for the production of higher hydrocarbons, methanol and synthesis gas from methane. Since 1982, the oxidative coupling of methane (OCM) to produce ethylene and higher hydrocarbons has received world-wide attention as a potentially interesting process for upgrading natural gas.[53] In the OCM process, methane and oxygen are fed over a metal or metal oxide catalyst at moderate temperatures (500-800 ^{o}C) to give higher hydrocarbons. However, this selective transformation of methane into C_n-hydrocarbons ($n \geq 2$) encounters many challenges because it requires high temperatures, high pressures, the necessity of special catalysts, etc. As an alternative to conventional heating, applying the MW heating technology to the OCM process offers a potential solution to these problems.

A comprehensive study comparing CH and MW heating in the oxidative coupling of methane has been done by Bond and co-workers[54] using various basic oxides. In this study it was found that the use of MW radiation resulted in C_2 formation occuring at much lower temperatures, and an increase in selectivity was also reported. Roussy *et al.*[55-57] also revealed an enhancement in C_2^+ selectivity with microwave irradiation of $(SmLiO_2)_{0.8}(CaO{-}MgO)_{0.2}$ catalysts, which they attributed to the gas being colder than the catalyst bed under microwave radiation. This indicates the formation of "hot spots" with temperatures very much in excess of the bulk catalyst that stimulate the reaction. Other researchers[58] who obtained similar results with $BaBiO_{3-x}$ and Li/MgO catalysts suggested that the electromagnetic field decreased the concentration of oxygen species at the catalytic surface and gas quenching at the outlet of the catalytic bed. Zhang *et al.*[59] have studied methane conversion and C_2 yields as a function of temperature under both heating methods in the absence of oxygen. In their findings they noted that the production of ethane using MW heating occurred at temperatures some 250 ^oC below the temperature at which ethane was first detected under conventional heating.

1.2.3.2 Decomposition of hydrogen sulfide

The catalytic conversion of hydrogen sulfide (H_2S) into hydrogen and sulfur is commercially important for the coal and petrochemical industry.[60] H_2S is a by-product from the sweetening of sour natural gas, the hydrodesulphurization of light hydrocarbons, and from the upgrading of heavy oils, bitumens and coal. On its own, H_2S has restricted industrial applications and it causes damage to the environment since it is a strong acid pollutant. However, it has a potentially high economic value if both the sulfur and hydrogen gas can be recovered. Hydrogen finds many applications in industry, for example, in hydrocracking and in hydrotreating to produce fuels, in the synthesis of ammonia and methanol, and in fuel cells.

The basic equation for H_2S decomposition is given by the equation;

$$H_2S_{(g)} \leftrightarrow H_{2(g)} + 1/2S_{2(g)} \qquad H^{\theta} = 84.8 \text{ kJmol}^{-1} \qquad (1.4)$$

As seen from the balanced equation, the reaction is highly endothermic and it is associated with relatively low conversion efficiencies even if the reaction is performed at high

temperatures. Numerous procedures are being developed to enhance this decomposition process,[61,62] and microwave-assisted decomposition of hydrogen sulfide is one possible solution.

Zhang and co-workers[63] have studied the microwave-assisted decomposition of H_2S on molybdenum sulfide/γ-alumina (impregnated or mechanically mixed) catalysts, using an optical fibre thermometer to monitor the temperature. A comparison of the conversion efficiency for the different catalysts under microwave and conventional thermal conditions is shown in Figure 1.7. Calculated equilibrium conversion efficiencies are also included for comparison. The results obtained using conventional heating conditions are in good agreement with the equilibrium data. On the other hand, results obtained under microwave conditions give much higher conversions compared to both the conventional heating and the calculated equilibrium conversions. This suggests the existence of high temperatures in some catalyst bed sites compared to the average temperature measured.[9] This is evidence for the presence of "hot spots".[54]

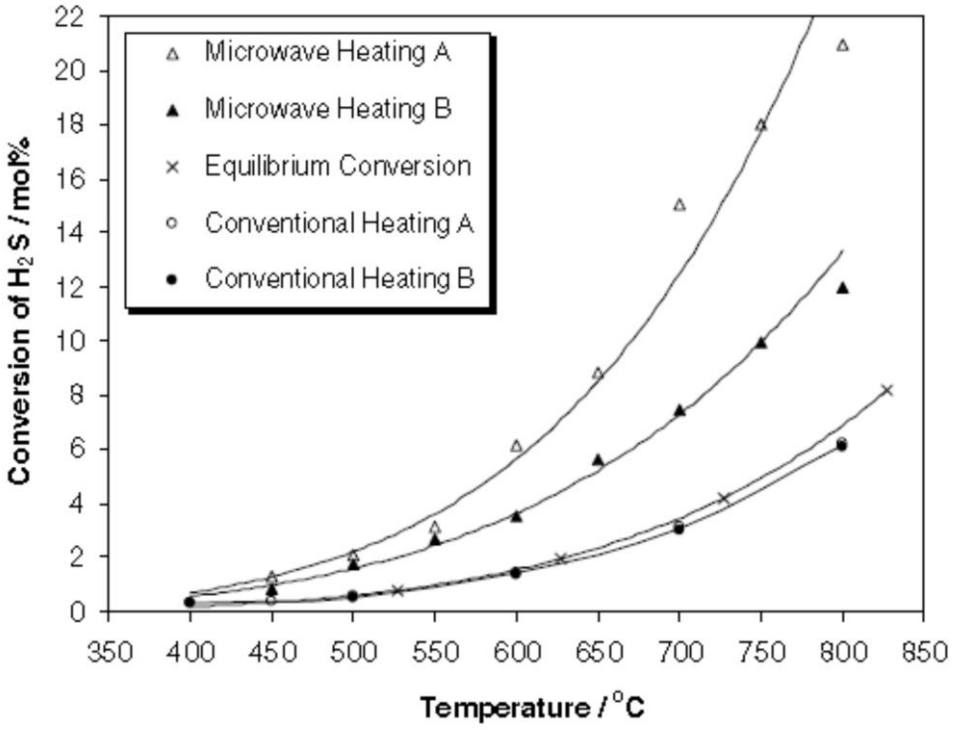


Figure 1.7 H_2S conversion as a function of temperature for (A) mechanically mixed catalyst and (B) an impregnated catalyst, under microwave and conventional heating conditions.[63]

In Figure 1.7, the presence of hot spots was used to explain the higher efficiency produced by the mechanically mixed catalyst (A) compared to the impregnated one (B) when microwave heating was studied. This is because under microwave heating conditions, the poorly dispersed mechanical catalyst was more likely to accentuate the hot-spot phenomenon, either because there was a higher concentration of hot spots or because the hot spots had a higher temperature.

1.2.3.3 Fischer-Tropsch Synthesis

Fischer-Tropsch synthesis (FTS) is a surface catalysed chemical reaction in which synthesis gas (syngas), a mixture of carbon monoxide and hydrogen, is converted into a mixture of hydrocarbons. These hydrocarbons are then used in the production of synthetic fuels for running trucks, cars and jet engines. Current research in FTS aims to optimise the activity and the selectivity of the process. This is normally achieved by modifying the support, increasing the activity of the active metal on the support, promoting the catalyst by the addition of a metal (e.g. potassium), improving the preparation method[64] or even by applying the microwave heating technology to the process.

Reubroycharoen *et al.*[65] have applied the advantages offered by microwave heating to the synthesis of highly active Co-based Fischer Tropsch catalysts. Instead of calcining their catalysts conventionally, the authors calcined them using microwave radiation. As a result, monodispersed catalysts were obtained and the agglomeration associated with conventional calcination was not witnessed in these catalysts (Figure 1.8). The catalysts that were calcined using microwave irradiation also displayed much higher catalytic activities in Fischer-Tropsch synthesis when compared to their conventionally calcined counterparts. A CO conversion of 69% and a chain-growth probability α value of 0.85 was obtained under conventional drying, while 14 minutes of microwave drying gave a CO conversion of about 82% and a chain-growth probability of 0.88. The differences in the catalyst properties were attributed to the volumetric heating nature of microwaves, which gives uniform heating. Liu and co-workers[66] also reported similar microwave effects on V_2O_5/SiO_2 catalysts that are used in the oxidation of *o*-xylene to phthalic anhydride. Microwave heating was also used in catalyst preparation, even in these catalysts.

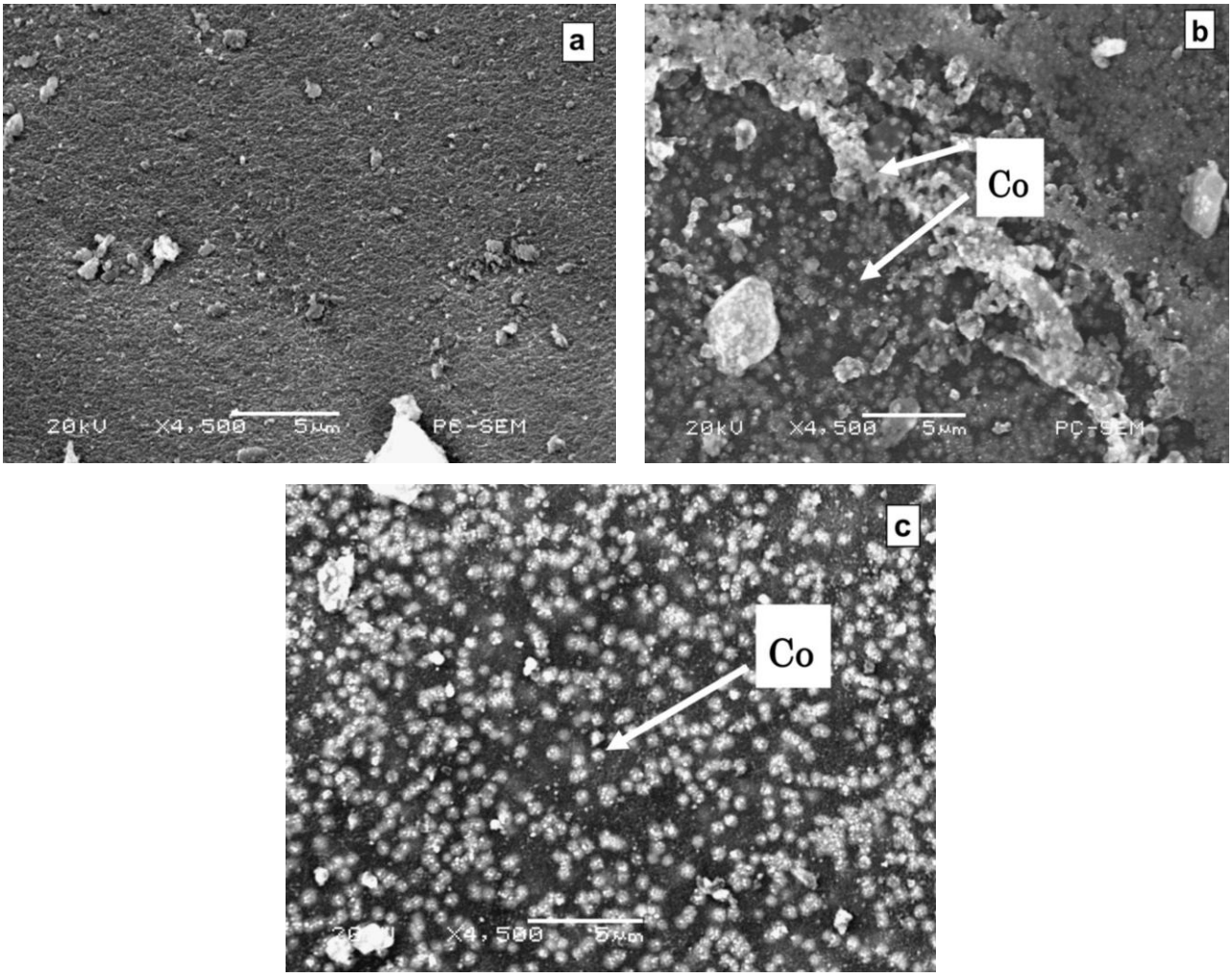


Figure 1.8 SEM images of Co/SiO_2 catalysts (20kV, x4,500): (a) Silica support, (b) conventional heating catalyst and (c) microwave irradiation catalyst.[65]

Recently, studies done by Linganiso[67] in our laboratories showed that microwave pre-treatment of Fischer-Tropsch catalysts in the solid-state improved the catalyst's properties. Using Secondary Ion Mass Spectrometry (SIMS) it was shown that the surface Fe:K ratio changed from 0.055 to 0.095 after microwave pre-treatment. This change in surface composition is believed to be caused by the migration of potassium ions to the iron surface during microwave irradiation. These results form the starting point for the work done in this study.

Linganiso also showed that the number and types of active sites present on the surface of the catalyst were increased by microwave pre-treatment. This was established by the temperature programmed surface reaction (TPSR) technique. The Fischer-Tropsch activity of these catalysts showed marked improvements in carbon dioxide selectivity and olefin formation after microwave pre-treatment, while methane selectivity simultaneously decreased. These rate enhancements were attributed to the promotional manner in which microwaves affected the iron and potassium interaction.

1.3 Concluding remarks

The principal question which microwave chemists ask is: Why is a category of reactions like the esterification of fatty acids, the acylation of aromatic ethers or Diels-Alder reactions accelerated by microwaves, while other reactions like the arylation of alkenes, the hydrolysis of sugars or the cyclisation of citronella are not accelerated by microwaves.[68] Regardless of the relatively large body of published work in this area,[69-71] the exact reasons as to how microwave irradiation is able to enhance chemical processes is still unknown. A substantial number of literature reports are based on inaccurate or unfounded comparisons with classical conditions which do not enable unequivocal conclusions to be made about microwave effects. Thus often some contradictions and controversies have appeared in the literature.[72-76]

A widespread explanation given for MW heating is the so-called "specific-" or "nonthermal-" microwave effect. The effect is defined as *accelerations or alterations of chemical transformations in a microwave field that can not be achieved or duplicated by conventional heating, but essentially are still thermal effects.*[1] This category includes, for example, (i) the superheating effect of solvents at atmospheric pressure, (ii) the selective heating of, e.g., strongly microwave absorbing heterogeneous catalysts or reagents in less polar reaction media, and (iii) the elimination of wall effects caused by inverted temperature gradients.[12]

1.4 Aims and objectives

The study was undertaken to investigate the effect of potassium on microwave modified FT catalysts. It was also in the interest of this work to verify if iron-based FT catalysts can indeed be modified by microwave pre-treatment. The specific objectives of this work are as follows:

- To determine and optimise the correlation between the loading of potassium in a catalyst and the effect of microwave pre-treatment, if it does exist.

- To characterise in detail the microwaved and the non-microwaved catalysts using Brunauer-Emmett-Teller (BET) surface area, powder X-ray diffraction (PXRD), temperature programmed reduction (TPR), X-ray fluorescence (XRF), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). Data obtained from the study should provide information on the catalyst's surface area, morphology and reducibility.

- To test the surface reactivity and performance of the microwaved and the non-microwaved catalysts using temperature programmed surface reaction-mass spectroscopy (TPSR-MS) and the Fischer-Tropsch reaction.

- To investigate if microwave modification of FT catalysts is influenced by a support. This was achieved by comparing data recorded from silica supported and unsupported catalysts.

- To study the effect of the microwave pre-treatment time on both supported and unsupported catalysts.

- To synthesise, characterise and test the effect of microwave pre-treatment on catalysts with varying particle sizes. This would be achieved by comparing catalysts that were prepared using incipient wetness impregnation versus those prepared using the deposition precipitation technique.

- To verify if physisorption and chemisorption of CO on iron-based FT catalysts is influenced by the modification of the catalysts using microwaves. This was achieved by performing methanation studies using the TPSR technique.

1.5 References

(1) Kappe, C. O.; Dallinger, D.; Murphree, S. S. *Practical microwave synthesis for organic synthesis*; Wiley-VCH: Weinheim, 2009.

(2) Harver, A. F. *Microwave Engineering*; Academic Press: New York, 1963.

(3) Neas, E. D.; Collins, M. J. *Introduction to microwave sample preparation theory and practice*; American Chemical Society: Washington, DC, 1988.

(4) Hayes, B. L. *Microwave synthesis, chemistry at the speed of light*; CEM Publishing: Mathews, NC, 2002.

(5) Holcombe, C. E., Dykes, N.L. *J. Matter. Sci.* **1991**, *26*, 3730.

(6) Gammampila, K., Dunscombe, P.B., Southcott, B.M., Stacey, A.J. *Clin. Phys. Physiol. Meas.* **1981**, *2*, 285.

(7) Caddick, S. *Tetrahedron* **1995**, *51*, 10403.

(8) Whittaker, A. G., Mingos, D.M.P. *Chemistry under extreme or non-classical conditions*; 1st ed.; Wiley, 2002.

(9) Zhang, X.; Hayward, D. O. *Inorganica Chimica Acta* **2006**, *359*, 3421.

(10) Mutyala, S.; Fairbridge, C.; Pare, J. R. J.; Belanger, M. R.; Ng, S.; Hawkins, R. *Fuel Process. Technol.* **2010**, *91*, 127.

(11) Silverwood, I. P. Ph.D. Thesis, University of Edinburg, 2006.

(12) Kappe, C. O.; Stadler, A. *Microwaves in organic and medicinal chemistry*; Wiley-VCH: Weinheim, 2005.

(13) Kappe, C. O. *Angew. Chem. Int. Ed.* **2004**, *43*, 6250.

(14) Hoffmann, J.; Nuchter, M.; Ondruschka, B.; Wasserscheid, P. *Green Chem.* **2003**, *5*, 296.

(15) *Evalueserve's special report on Developments in microwave chemistry*; Chemistry World, April 2005; Vol. 2 (4).

(16) Bilecka, I.; Niederberger, M. *Nanoscale* **2010**, *2*, 1358.

(17) Thostenson, E. T.; Chou, T. W. *Composites: Part A* **1999**, *30*, 1055.

(18) Palaith, D.; Silberglitt, R. In *American Ceramic Society Bulletin* 1989; Vol. 69, p 1601.

(19) Will, H.; Scholz, P.; Ondruschka, B. *Chem. Eng. Technol.* **2004**, *27*, 113.

(20) Varma, R. S. *Green Chem.* **1999**, *1*, 43.

(21) Gedye, R.; Smith, F.; Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L.; Rousell, J. *Tetrahedron Lett.* **1986**, *27*, 279.

(22) Giguere, R. J.; Bray, T. L.; Duncan, S. M.; Majetich, G. *Tetrahedron Lett.* **1986**, *27*, 4945.

(23) Ripley, E. B. In *US Patent no.: 3742208, International Patent no.: AG01K108FI.*

(24) Colacino, E.; Lamaty, F.; Martinez, J.; Parrot, I. *Tetrahedron Lett.* **2007**, *48*, 5317.

(25) Wawrzyniak, P.; Heinicke, J. *Tetrahedron Lett.* **2006**, *47*, 8921.

(26) Pereira, M.; Thiery, V.; Besson, T. *Tetrahedron Lett.* **2007**, *48*, 7657.

(27) Nuchter, M.; Ondruschka, B.; Bonrath, W.; Gum, A. *Green Chem.* **2004**, *6*, 128.

(28) Kremsner, J. M.; Kappe, C. O. *J. Org. Chem.* **2006**, *71*, 4651.

(29) Bacsa, B.; Horvati, K.; Bosze, S.; Andreae, F.; Kappe, C. O. *J. Org. Chem.* **2008**, *73*, 7532.

(30) Obermayer, D.; Kappe, C. O. *Org. Biomol. Chem.* **2010**, *8*, 114.

(31) Kappe, C. O. *Chem. Soc. Rev.* **2008**, *37*, 1127.

(32) Bacci, M.; Bini, M.; Checcucci, A.; Ignesti, A.; Millanya, L.; Rubino, N.; Vanni, R. *J. Chem. Soc., Faraday. Trans.* **1981**, *77*, 1503.

(33) Williams, N. H. *J. Microwave Power* **1967**, *2*, 140.

(34) Baghurst, D. R.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1992**, 674.

(35) de la Hoz, A.; Diaz-Ortiz, A.; Moreno, A. *Chem. Soc. Rev.* **2005**, *34*, 164.

(36) Deshayes, S.; Liagre, M.; Loupy, A.; Luche, J. L.; Petit, A. *Tetrahedron* **1999**, *55*, 10851.

(37) Loupy, A.; Petit, A.; Hamelin, J.; Texier-Boullet, F.; Jacquault, P.; Mathe, D. *Synthesis* **1998**, *9*, 1213.

(38) Melucci, M.; Barbarella, G.; Sotgiu, G. *J. Org. Chem.* **2002**, *67*, 8877.

(39) Melucci, M.; Barbarella, G.; Zambianchi, M.; Di Pietro, P.; Bongini, A. *J. Org. Chem.* **2004**, *69*, 4821.

(40) Alesi, S.; Di Maria, F.; Melucci, M.; Macquarrie, D. J.; Luque, R.; Barbarella, G. *Green Chem.* **2008**, *10*, 517.

(41) Strauss, C. R.; Trainor, R. W. *Aust. J. Chem.* **1995**, *48*, 1665.

(42) Raner, K. D.; Strauss, C. R.; Trainor, R. W. *J. Org. Chem.* **1995**, *60*, 2456.

(43) Nilsson, P.; Larhed, M.; Hallberg, A. *J. Am. Chem. Soc.* **2001**, *123*, 8217.

(44) Kaval, N.; Dehaen, W.; Kappe, C. O.; Van der Eycken, E. *Org. Biomol. Chem.* **2004**, *2*, 154.

(45) Hosseini, M.; Stiasni, N.; Barbieri, V.; Kappe, C. O. *J. Org. Chem.* **2007**, *72*, 1417.

(46) Loupy, A.; Maurel, F.; Sabatie-Gogova, A. *Tetrahedron* **2004**, *60*, 1683.

(47) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612.

(48) Agostiano, A.; Catalano, M.; Curri, M. L.; Monica, M. D.; Manna, L.; Vasanelli, L. *Micron* **2000**, *31*, 253.

(49) Horikoshi, S.; Abe, H.; Torigoe, K.; Abe, M.; Serpone, N. *Nanoscale* **2010**, *2*, 1441.

(50) Dresselhaus, M. S.; Dresselhaus, G.; Avouris, P. In *Topics in Applied Physics*; Springer-Verlag: Berlin, 2001.

(51) Frank, S. *Science* **1998**, *280*, 1744.

(52) Tanashev, Y. Y.; Fedoseev, V. I.; Aristov, Y. I.; Pushkarev, V. V.; Avdeeva, L. B.; Zaikovskii, V. I.; Parmon, V. N. *Catal. Today* **1998**, *42*, 333.

(53) Keller, G. E.; Bhasin, M. M. *J. Catal.* **1982**, *73*, 9.

(54) Bond, G.; Moyes, R. B.; Whan, D. A. *Catal. Today* **1993**, *17*, 427.

(55) Roussy, G.; Pearce, J. A. *Foundations and industrial applications of microwave and radio frequency fields*; Wiley: New York, 1995.

(56) Roussy, G.; Thiebaut, J. M.; Souiri, M.; Marchal, E.; Kiennemann, A.; Maire, G. *Catal. Today* **1994**, *21*, 349.

(57) Roussy, G.; Marchand, C.; Thiebaut, J. M.; Souiri, M.; Kiennemann, A.; Petit, C.; Maire, G.; Vol. French Patent no. 2696447, US Patent no. 08.131.428.

(58) Roussy, G.; Marchal, E.; Thiebaut, J. M.; Kiennemann, A.; Maire, G. *Fuel Process. Technol.* **1997**, *50*, 261.

(59) Zhang, X.; Lee, C. S. M.; Mingos, D. M. P.; Hayward, D. O. *Appl. Catal. A: Gen.* **2003**, *249*, 151.

(60) Kaloidas, V. E.; Papayannakas, N. G. *Ind. Eng. Chem. Res.* **1991**, *30*, 345.

(61) Zaman, J. *Fuel Process. Technol.* **1995**, *41*, 159.

(62) Getoff, N. *Int. J. Hydrogen Energy* **1990**, *15*, 407.

(63) Zhang, X. L.; Hayward, D. O.; Mingos, D. M. P. *Chem. Commun.* **1999**, 975.

(64) Iglesia, E. *Appl. Catal. A: Gen.* **1997**, *161*, 59.

(65) Reubroycharoen, P.; Vitidsant, T.; Liu, Y.; Yang, G.; Tsubaki, N. *Catal. Commun.* **2007**, *8*, 375.

(66) Liu, Y.; Lu, Y.; Liu, S.; Yin, Y. *Catal. Today* **1999**, *51*, 147.

(67) Linganiso, L. Z. PhD. Thesis, University of the Witwatersrand, 2008.

(68) Loupy, A. *Microwaves in organic synthesis*; 2nd ed.; Wiley-VCH: Weinheim, 2006; Vol. 1

(69) Baxendale, I. R.; Ley, S. V.; Nessi, M.; Piutti, C. *Tetrahedron* **2002**, *58*, 6285.

(70) Artman, D. D.; Grubbs, A. W.; Williams, R. M. *J. Am. Chem. Soc.* **2007**, *129*, 6336.

(71) Bogdal, D.; Penczek, P.; Pielichowski, J.; Prociak, A. *Adv. Polym. Sci.* **2003**, *163*, 193.

(72) Raner, K. D.; Strauss, C. R.; Vyskoc, F.; Mokbel, J. *J. Org. Chem.* **1993**, *58*, 950.

(73) Laurent, R.; Laporterie, A.; Dubac, J.; Lefeuvre, S.; Audhuy, M. *J. Org. Chem.* **1992**, *57*, 7099.

(74) Westaway, K. C.; Gedye, R. N. *J. Microwave Power Electromag. Energ.* **1995**, *30*, 219.

(75) Kuhnert, N. *Angew. Chem.* **2002**, *114*, 1943.

(76) Strauss, C. R. *Angew. Chem. Int. Ed.* **2002**, *41*, 3589.