



# Microwave radiation in the modification of iron Fischer–Tropsch catalysts



W.M. Dlamini<sup>a</sup>, N.J. Coville<sup>a</sup>, M.S. Scurrall<sup>b,\*</sup>

<sup>a</sup> Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

<sup>b</sup> Department of Civil and Chemical Engineering, University of South Africa, Florida, Johannesburg, South Africa

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## ABSTRACT

Potassium-promoted unsupported iron Fischer–Tropsch catalysts have been subjected to microwave radiation treatment as part of the catalyst preparation process. The treatment is applied after the catalysts have been dried and calcined. Solid-state modifications occur which result in changes in the manner and quantity of carbon monoxide adsorbed on the surface as detected by temperature programmed surface reaction (TPSR) with hydrogen. Methane is the essential product of the TPSR runs. The response to microwave treatment is an increase in the methane production at all potassium levels, but the magnitude of the increase is potassium-loading dependent and peaks at a potassium loading of 0.7 wt%. Microwave-induced changes in TPSR characteristics appear to result from selective heating occurring almost immediately on exposure of the catalysts to radiation. Longer duration of microwave exposure does not appear to result in further changes.

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## 1. Introduction

Industrial and domestic microwave operate at 915 MHz or 2.45 GHz (wavelength 32.8 or 12.2 cm, respectively) to avoid interfering with radar or telecommunication frequencies. Within this region of electromagnetic energy, only molecular rotations of molecules are affected by the radiation. Microwave energy consists of two components: an electric field and a magnetic field, though only the electric field transfers energy to heat a substance. The energy in microwave photons ( $9.65 \times 10^{-4}$ – $9.65 \times 10^{-2}$  kJ/mol) is very low relative to the typical energy required to cleave molecular bonds (335–500 kJ/mol) and therefore microwaves do not directly affect molecular structure. However, local heating effects and, in particular temperature gradients may be set up when exposing suitable solids to microwave radiation [1]. The physics of the effects are such that nanosized domains are expected to be more responsive to microwave-induced effects and so catalytic solids are likely to exhibit interesting characteristics.

Tremendous efforts are being made toward controlling the particle size, particle size distribution, shape, dispersion and structure of nanomaterials using the effective heating provided by microwave irradiation. Horikoshi et al. [2] have shown that

microwave 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 W microwave irradiation gave a  $0.51^\circ\text{C s}^{-1}$  heating rate, whereas for the oil-bath heating method a rate of  $0.09^\circ\text{C s}^{-1}$  was obtained at a power consumption of 400 W. Consequently, smaller particles with a fairly narrow particle size distribution (1.8–3.6 nm; average size  $\sim 3$  nm) were achieved under microwave heating, while conventional heating produced a broader particle size distribution of 1–5 nm.

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, with quantized resistance, independent of length due to its unique 1D structure [3]. 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 radiation, localized heating is observed thus promoting their removal from the CNT. In contrast, laboratory prepared CNTs have structural imperfections.

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,

\* Corresponding author.

E-mail address: [scurrrms@unisa.ac.za](mailto:scurrrms@unisa.ac.za) (M.S. Scurrall).

resistance to poisoning and degradation effects. Since the energy of microwave quanta is not sufficient to achieve direct electronic excitation of reagents or the breaking of chemical bonds, microwave heating is considered to be a probable way for activating solid catalysts.

Natural gas, which is between 70 and 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. In the OCM process, methane and oxygen are fed over a metal or metal oxide catalyst at moderate temperatures (500–800 °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 for special catalysts, etc. As an alternative to conventional heating, applying the microwave heating technology to the OCM process offers a potential solution to these problems.

A comprehensive study comparing conventional and microwave heating in the oxidative coupling of methane has been done by Bond et al. [4] using various basic oxides. In this study it was found that the use of microwave radiation resulted in  $C_2$  formation occurring at much lower temperatures, and an increase in selectivity was also reported. Roussy et al. [5] 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 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 [6]. Zhang et al. [7] 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 microwave heating occurred at temperatures some 250 °C below the temperature at which ethane was first detected under conventional heating.

The catalytic conversion of hydrogen sulfide into hydrogen and sulfur is commercially important for the coal and petrochemical industry. Hydrogen sulfide 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.  $H_2S$  splitting 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 [8,9] and microwave-assisted decomposition of hydrogen sulfide is one possible solution. On molybdenum sulfide/ $\gamma$ -alumina (impregnated or mechanically mixed) catalysts, using an optical fiber thermometer to monitor the temperature, experiments have revealed higher temperatures in some catalyst bed sites compared to the average temperature measured. This is evidence for the presence of “hot spots” and is associated with high reaction rates.

In Fischer–Tropsch synthesis (FTS) catalysis, Reubroycharoen et al. [10] 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 seen. 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  $\alpha$  value of 0.85 was obtained under conventional drying, while 14 min 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 et al. [11] reported similar microwave effects on  $V_2O_5/SiO_2$  catalysts that are used in the oxidation of *o*-xylene to phthalic anhydride.

Recently, studies reported by Linganis et al. [1] in our laboratories showed that microwave pretreatment of Fischer–Tropsch catalysts in the solid-state improved the catalytic 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 pretreatment. 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. In reviewing the earlier work the most significant changes in the catalysts were the surface composition as revealed by SIMS and the surface reactivity of carbon (probably as CO) when CO was preadsorbed and subsequently reacted with dihydrogen in TPSR experiments.

TPSR profiles were influenced by microwave radiation and the detailed structure proved to be a function of the radiation power level. The overall catalytic effects in separate flow reactor studies were (1) a slight increase in activity of FTS and WGS reactions, (2) a substantial decrease in methane selectivity, and (3) other changes in hydrocarbon product selectivity. We felt that the furthering of our understanding for these effects would best be served by a focus on the surface properties as monitored by TPSR of preadsorbed CO. According this paper investigates this aspect in some depth. We have confined our catalysts to unsupported iron. Unsupported (but fused) iron catalysts are used in the high productivity FTS installations operated in South Africa by SASOL. We have studied catalysts promoted with potassium at various levels since potassium was implicated in the earlier work as a probably vehicle for the influence of microwave radiation on the surface and catalytic behavior observed [1].

## 2. Experimental

Unsupported and silica supported iron catalysts were prepared in this study. The methodology used for each type of catalyst preparation is discussed below.

The K/Fe catalysts used in this study were prepared using the pH-controlled continuous precipitation procedure as described by Kölbl and Raleek. A 4 M solution of  $Fe(NO_3)_3 \cdot 9H_2O$  was precipitated by the drop-wise addition of 12 M  $NH_4OH$  to a pH of 7.2 with continuous stirring. The resultant slurry was stirred for an additional 15 min and the final pH was recorded. A centrifuge was used to separate the precipitate from the liquid. The centrifuge speed used was 5000 rpm and this was done for 15 min. The precipitate was then dried at room temperature for 12 h. Subsequently, the precipitate was kept at 120 °C for 12 h to remove water that was incorporated within the precipitate. Calcination was performed at 350 °C for 6.5 h using a heating rate of 10 °C/min.

For the promoted catalysts, appropriate amounts of  $K_2CO_3$  solutions were added to the calcined precursor via the incipient wetness

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