CHAPTER THREE

MICROWAVE CHEMISTRY

In this chapter, a brief background on microwave chemistry is reported. An introduction on the applications of microwave heating in solids and in catalysis is also reported briefly.

3.1 INTRODUCTION

Most of the recent reviews about microwave processes have focused on either synthesis of solid catalysts or sintering of these materials using microwave irradiation (Reubroycharoen et al., 2007; Agrawal et al., 2002). None of the reviews have specifically addressed the recent development of influencing catalytic activity and/or selectivity using the microwave pre-treatment. The present study focuses on microwave effects on catalytic activity and selectivity in Fischer-Tropsch synthesis (FTS). The activities and selectivities of the FT catalysts can be enhanced by modifying the support, increasing dispersion, promoting the catalysts, improving preparation method and by pre-treating the catalyst using the microwave oven.

In the microwave process, heat is generated internally within the material instead of originating from external sources so there is an inverse heating profile (Agrawal et al., 2002). The heating process is very fast because the material is heated by energy conversion rather than by energy transfer. Energy transfer takes place in conventional techniques via thermal conduction mechanisms.

The advantages of microwave heating include, time and energy saving, very rapid heating rates without damage due to thermal shock, reduced processing time and temperature and improved mechanical properties (Roy et al., 1985).

Microwave heating has also been found to have an amazing capability of accelerating chemical reactions. Successful demonstrations of the use of microwave include organic and inorganic synthesis (Bose et al., 1997), mineral digestion (Park, 2000) and extraction (Oberhagemann et al., 1999). Oberhagemann and the co-workers discovered in their work that the use of microwave in hydrothermal synthesis of ceramic powders has achieved kinetic acceleration by one to two orders of magnitude (Oberhagemann et al., 1999) whereas microwave assisted chlorine leaching of copper minerals at reflux temperature has achieved about three times enhancement (Ding, 1997). The study showed that the microwave hydrothermal leaching is a very rapid process compared with thermally heated process.

Scurrell et al. also discovered that there are benefits of microwave pre-treatment for Zn-ZSM-5 catalyst prepared by solid-state ion exchange method (Scurrell et al., 2002). They also reported that there are effective benefits in the preparation of solid catalyst using the microwave. This project aims to use microwave catalyst pre-treatment and to compare results obtained with those found with conventional heating.

3.2 MICROWAVE EFFECT IN THE SYNTHESIS AND SINTERING OF SOLID MATERIALS

Microwave irradiation has been used in sintering of solid materials. Roy et al. reported that it is possible to sinter the ferroic materials at amazingly low temperatures, between 300 ^{o}C and 700 ^{o}C in 5-12 minutes with the microwave process whereas conventional method for the synthesis of ferroic phases requires temperatures in the range 900 ~ 1450 ^{o}C and several hours soaking time (Roy et al., 1997). They also reported that synthesis of ferroelectric titanates based on conventional ceramic methods involve long reaction times due to slow diffusion rates in the solid state (Glazer et al., 1978).

Work done by Agrawal and the co-workers involved the use of the microwave oven at 2.45 GHz in the preparation and sintering of barium titanate (BT) (Agrawal et al., 2002). Appropriate amounts of $BaCO_3$ and TiO_2 were used as starting materials for the synthesis. $BaTiO_3$ phase was obtained by heating the precursors in a multimode microwave capacity at 1450 ^oC for just 25 minutes (Agrawal et al., 2002). The results showed that the microwave method takes only a fraction of the time required in conventional processing to achieve single-phase dense material. This is evidence that the microwave saves time.

Their results included SEM results, which showed that the microwave method avoids undesirable grain growth and provides a finer and more uniform microstructure, this was found to be due to the rapidity of the microwave method. The microwaved samples showed less porosity than conventional ones. Trans-granular fracture was also observed for the microwave processed BT samples, this was reported to be due to the grain boundaries being narrow and not containing sufficient defects such as porosity to produce inter-granular fracture. In their findings they concluded that the microwave method is simple, fast and energy efficient compared with conventional methods (Agrawal et al., 2002).

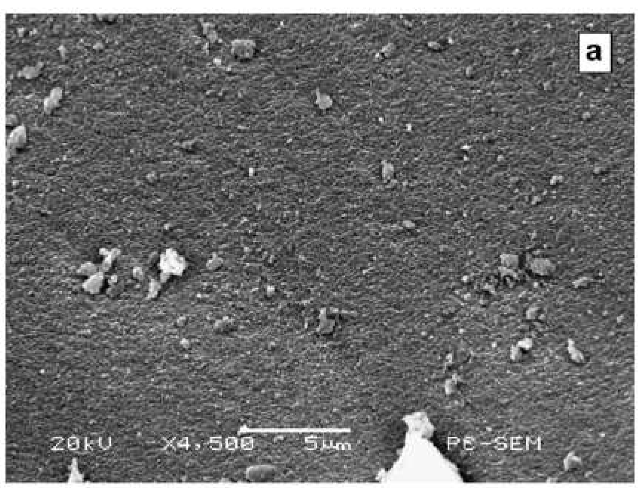
3.3 MICROWAVE EFFECT IN CATALYSIS

The effect of microwave in synthesis and sintering of powders such as alumina is well accepted whereas microwave effect in catalysis has not been widely studied. Microwave method of catalyst preparation has been used in the preparation of cobalt Fischer-Tropsch catalysts (Reubroycharoen et al., 2007).

Microwave irradiation has been effectively applied in the preparation of highly active Fischer-Tropsch catalysts and other solid catalysts. The advantages of microwave irradiation over conventional heating are as follows: rapid drying, uniform particle size and better distribution (Reubroycharoen et al., 2007).

Other work includes that of Liu et al. who discovered that V_2O_5/SiO_2 catalysts prepared by microwave irradiation were more active than those prepared by conventional heating (Liu et al., 1999). The high activity of such catalysts was reported to be due to the homogeneous dispersion of V_2O_5 on the surface of SiO_2. Microwave irradiation was also found to reduce segregation of the particles to grains (Liu et al., 1999).

Reubroychoroen and the co-workers reported that the microwave catalyst showed better distribution of the Co particles on silica surface (**figure. 3.1c**) compared to that of the conventional heating catalyst (**figure. 3.1b**) in their work titled 'highly active Fischer-Tropsch synthesis Co/SiO_2 catalysts prepared from microwave irradiation'. In addition, they mentioned that Co particles in the conventional heating catalyst partly agglomerate on the surface and showed non-uniform distribution. Scanning electron microscopy (SEM) results are shown in **figure 3.1**.



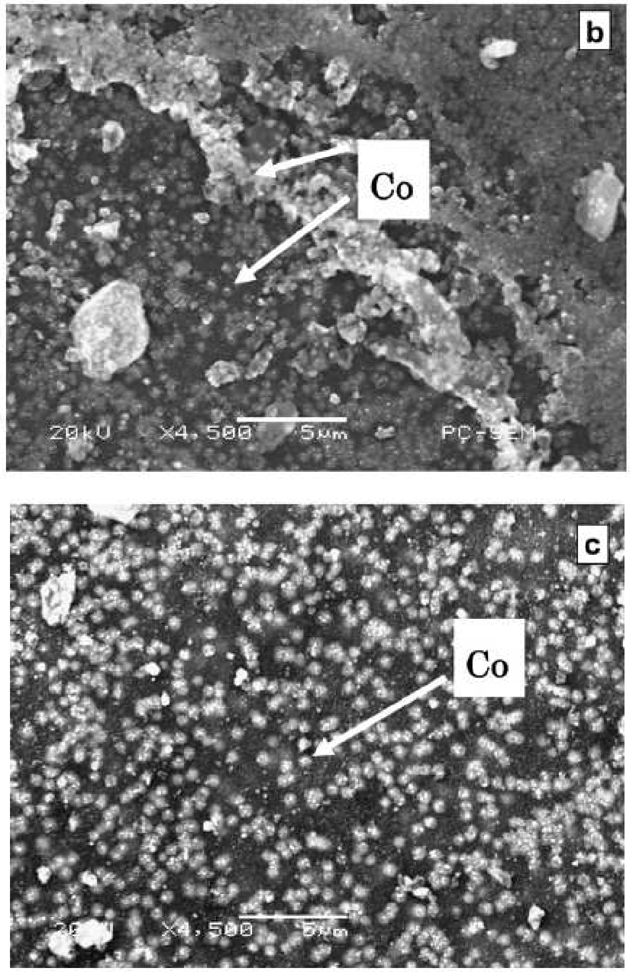


Figure 3.1: SEM images of Co/SiO_2 catalysts (20kV, x4, 500): (a) silica support, (b) conventional heating catalyst and (c) microwave irradiation catalyst (Reubroycharoen et al., 2007).

Their findings included XRD results which showed that the conventionally heated catalyst exhibited the highest intensity of Co_3O_4 pattern peaks whereas the microwave heating catalysts showed a slight increase in intensity due to an increase in irradiation time. Product selectivity (CH_4 and CO_2) is also affected by the microwave irradiation (**table 3.1.**).

Table 3.1 Catalytic activity of conventional and microwave cobalt catalysts on Fischer-Tropsch synthesis (FTS).

Irradiating time (min]	CO conv. (%]	Selectivity (%)		α	XRD (nm]
		CH_4	CO_2		
0[a]	69.0	7.7	4.5	0.85	13.50
4	71.3	3.5	1.4	0.88	9.75
10	78.4	5.1	3.1	0.88	10.50
14	81.7	8.1	6.1	0.88	10.50
45	81.2	7.9	6.9	0.88	11.25

Reaction condition: 1 g. of 10 wt% Co/SiO_2, 513 K, 1.0 MPa, W/F = 10.0 g cat h/mol.

[a] Conventional heating method.

The activity and selectivity of the catalyst can be improved by microwave irradiation. The study undertaken aims to examine the behaviour of a microwave pre-treated catalyst in Fischer-Tropsch synthesis. We have pursued the irradiation of solid materials, rather than solutions or dispersions as have been investigated by others (Reubroycharoen et al., 2007). We observe any changes in catalytic activity and product selectivity due to microwave pre-treatment.

3.4 HOW DOES MICROWAVE IRRADIATION PROVIDE HEATING?

Microwaves are defined as electromagnetic waves with wavelengths ranging from 1 m down to 1mm with frequencies between 0.3 GHz and 300 GHz. Microwaves have three characteristics:

- They are reflected by metal,
- They pass through glass, paper, plastics,
- They are absorbed by food.

Microwaves are produced inside the oven by an electron tube called a magnetron. They are then reflected within the metal interior of the oven where they are absorbed by food. Food with high water content can be cooked more quickly than other foods because the microwave causes the water molecules to vibrate, producing heat that cooks food.

The energy of the microwave is converted to heat as it is absorbed by food. The food after being cooked by the microwave does not show any contamination. The microwaves cooks the outer layer first, the inside is cooked by heat conduction from the outer layer.

When Fischer-Tropsch catalysts are microwave pre-treated, the same thing applies, a catalyst with high water content will tend to absorb more microwaves than a dry iron catalyst. The microwave effect was found to be prominent on catalysts containing water. Microwave heating is more energy efficient than conventional heating because the microwave medium absorbs the heat faster and the energy heats only the catalyst and not the oven compartment.

In the case of iron catalyst, not all iron phases are good absorbing mediums. Magnetite is a good microwave absorber whereas hematite is not, because, magnetite is magnetic and hematite is diamagnetic.

3.5 THE EXPECTED BENEFITS OF MICROWAVE HEATING ON FISCHER-TROPSCH SYNTHESIS

Expected benefits of microwave in Fischer-Tropsch synthesis are as follows:

- Save time when heating the catalyst with microwave than conventional heating.
- Save heat as the microwaves heat only the catalyst and not whole oven compartment.
- Additional chemically induced effects on activity and selectivity might result.