Frequency Effects in the Catalytic Oligomerization of Methane via Microwave Heating

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Microwave radiation has been used to catalytically activate methane for oligomerization to higher hydrocarbons. The effect of frequency of microwave radiation on the microwave field distribution pattern and, consequently, on the product distribution for the methane reaction has been studied. Nickel catalysts, in the form of branched-type filaments, were used in these studies. Experiments were done with pure methane and using He as diluent. In general, as power increases, conversion of methane increases and selectivity toward C_{2s} decreases. At 4.60 GHz, as power increases from 130 to 370-W, selectivities of ethylene and ethane decrease and selectivity of acetylene increases. As power increases, selectivity toward benzene also increases. These data differ from the case at low frequency (2.45 GHz), in which the presence of He helped to prevent the formation of acetylene at all power levels. Changes in product distribution due to changes in frequency have been observed. For the case of methane both with and without diluent, as frequency increases from 2.40 to 4.60 GHz at 370 W, selectivity toward benzene also increases. When He was used as a diluent gas, as frequency increases, selectivity toward ethylene and acetylene also increases. When pure methane was used, the opposite was observed. These changes in product distribution due to changes in frequency might be related to different transverse magnetic modes at different frequencies. Different transient heating patterns may occur at different values of frequency. © 2001 Elsevier Science

1. INTRODUCTION

Many efforts have been focused on the activation of methane to more valuable products in the last two decades. Many studies have been done in order to produce more-valuable products from natural gas, of which methane is the major constituent. Natural gas is an inexpensive and abundant energy resource. Therefore, effective and economic processes to obtain higher hydrocarbons, methanol, and/or synthesis gas would be valuable.

The use of natural gas as an oil substitute could be possible if methane is converted into petrochemical species or gasoline components. This goal has been actively pursued by many groups around the world.

Thermal (1–3), homogeneous (4–6), and heterogeneous (7–10) catalytic conversion of methane to higher hydrocarbons have been studied by many authors. Due to the high thermodynamic stability of methane compared with that of higher hydrocarbons, methane can only be thermally converted to C_{2+} hydrocarbons at temperatures higher than 1400 K. The products are unsaturated and unstable hydrocarbons, such as acetylene. Therefore, appropriate temperature, residence time control, and rapid reaction quenching are necessary to achieve selectivity to desired products. Otherwise, carbon and hydrogen will be the only products.

Most recent efforts have been focused on the development of direct methane conversion by means of oxidative coupling into ethane and ethylene (4, 11). Other processes have been used for the activation of methane. Some of these involve electrochemical activation of methane, photocatalytic oxidation of methane, electrical discharges (12), partial oxidation of methane over redox catalysts, catalytic reactions involving transition metal complexes (3, 9–10, 12–19), microwave plasmas (20–24), and microwave heating (25–35).

Microwave energy interacts with materials at the molecular level. During microwave heating of a dielectric, internal electric fields are generated within the material. Such fields can produce translation of electrons and ions causing rotation of charged species. This movement can be opposed by friction, inertia, and other forces that can lead to attenuation of the electric fields, and to volumetric heating of the material (36). The ability of the microwave electric field to polarize molecules and the ability of these molecules to follow the rapid reversal of the electric field results in the conversion of electromagnetic energy into heat within the irradiated material.

The use of microwave heating to induce chemical reactions has been studied for several years. Over the past decade microwave heating has been employed extensively in organic (37–41) and inorganic synthesis (41–55).

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Microwave-induced catalytic reactions have been studied extensively by Wan and co-workers (25, 27–29, 35) and others (58–61). We have studied the oligomerization of methane to higher hydrocarbons using Ni powder, Fe powder, and activated carbon (62). Oligomers ranging from C_2 to C_6 hydrocarbons have been produced in a relatively high selectivity, depending on the nature of the catalyst, power level, and presence of He as a diluent gas.

Nickel catalysts have been shown to be highly selective and effective in lowering the activation energy for breaking the carbon–hydrogen bond. Although microwave heating has been studied very systematically for the oligomerization of methane, it is not clear yet what other factors might affect the activity and product distribution of this reaction. In this work, we studied the systematic effects of frequency and magnitude of the applied microwave radiation on the conversion and product distribution of methane oligomerization using nickel catalysts in the presence and absence of He as a diluent gas.

2. EXPERIMENTAL SECTION

2.1. Microwave Apparatus and Gas System

Oligomerization of methane was carried out in a flow reactor system. A Lambda Technologies variable frequency unit, Vari-Wave model VW-2750, was used for these experiments. Microwave radiation was transmitted from the magnetron to the cavity by means of a coaxial cable. The power level that can be achieved with this unit is from 0 to 500 W. There is an interlocked bulkhead SC-type connector designed to prevent any transmission of microwave energy until the cable has been firmly and correctly attached. The reactor, a straight 3/8-in. quartz tube, was mounted horizontally inside the cavity (Fig. 1). Methane gas as well as He diluent gas was mixed in a panel when necessary and flowed into the quartz reactor. Details of the experimental setup have been described elsewhere (62). High purity grade methane obtained from Matheson and ultra high purity helium purchased from Airgas were used.

Various frequencies and modes were produced in the microwave cavity. This cavity allows TM_{01n} modes ($n = 2$–9) over a frequency range of 2.400–5.056 GHz. The cavity was designed by Lambda Technologies to have different modes for each frequency. In Fig. 2 we show how these transverse magnetic modes were distributed in the cavity and the value of frequency that corresponds to each TM mode. Our experiments were done with and without diluent at 2.40 GHz at TM_{012} and also at 4.60 GHz at TM_{018} for comparison. Thermal paper was inserted into the microwave cavity and used to map the heating patterns of the various modes.
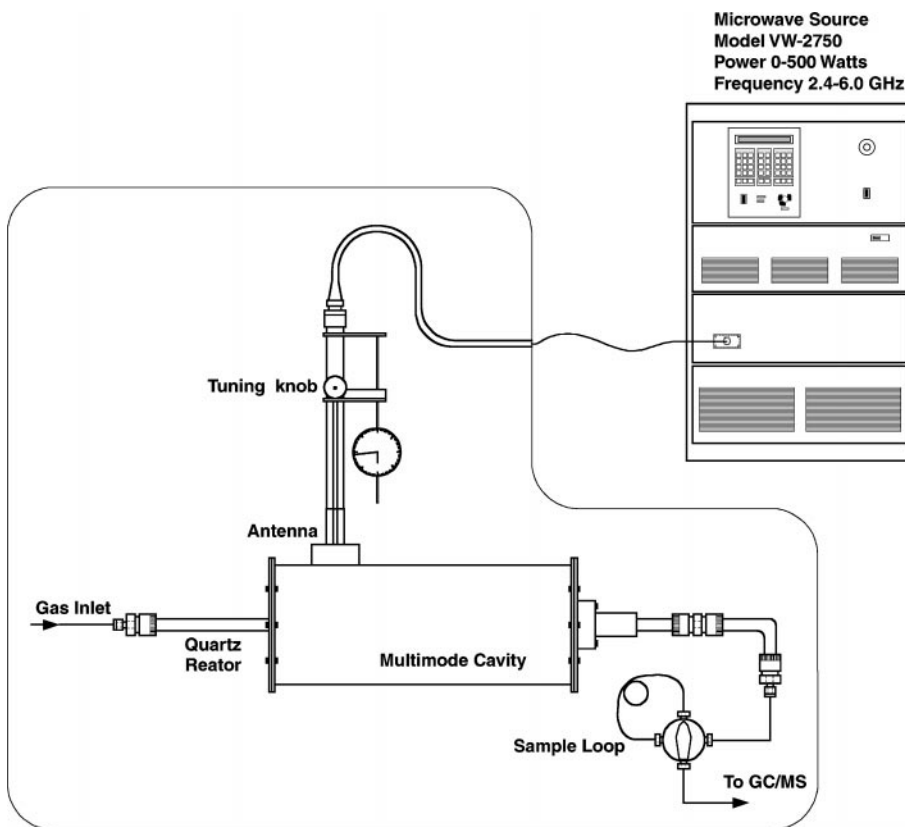

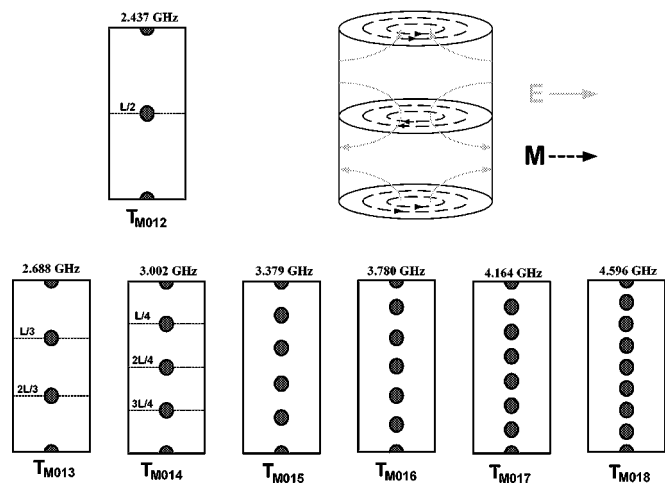FIG. 1. A microwave cavity and variable-frequency microwave apparatus.

FIG. 2. Transverse magnetic modes (TM_{01n}, $n = 2$–8) for the variable-frequency microwave cavity.

The length of the aluminum cavity was 29.5 cm and the radius was 5.15 cm. There was a tuning knob and antenna perpendicular to the length of the cavity (Fig. 1). In order to ensure microwave absorption for a specific frequency value and power level, the reflected power had to be minimized first by means of the tuning knob and the frequency tuning control on the main panel. Therefore, the working frequency is a result of the tuning process. Reflected power higher than 60 W makes the safety feature of the unit shut off. Thus, not all frequencies are possible for a particular system.

2.2. Catalyst

Nickel powder catalyst with morphology of branched filaments was used for these experiments. The diameters of the filaments were 2.5 μm, as measured in a scanning electron microscopy (SEM) photograph. Clusters of nickel metal particles were aggregated to form the filaments (Fig. 3). The oligomerization of methane was carried out in a 3/8-in. quartz reactor, which was placed inside the cavity. This catalyst was purchased from Inco Co. and was used as received. The catalyst (100 mg) was placed inside the reactor with high purity quartz wool on either side of the catalyst bed. The reactor was placed in the center of the aluminum cavity. Helium was flushed for 30 min through the reactor to purge the atmosphere.

The experiments were run at two different flow rates: 3 ml/min of pure methane; and 12 ml/min of a 3 : 1 mixture of helium and pure methane, respectively, at atmospheric pressure. Samples for analyses were taken after 3 min of irradiation at each power level (100, 130, 170, 210, 300, and 370 W).

2.3. Product Analysis

Products were trapped using a four-way gas sampling valve and analyzed by using an HP5890 Series II chromatograph equipped with a mass detector. Details about the gas chromatographer/mass spectrometer have been published elsewhere (62).

A carbon balance was used to estimate total conversion. All the compounds multiplied by the number of carbon
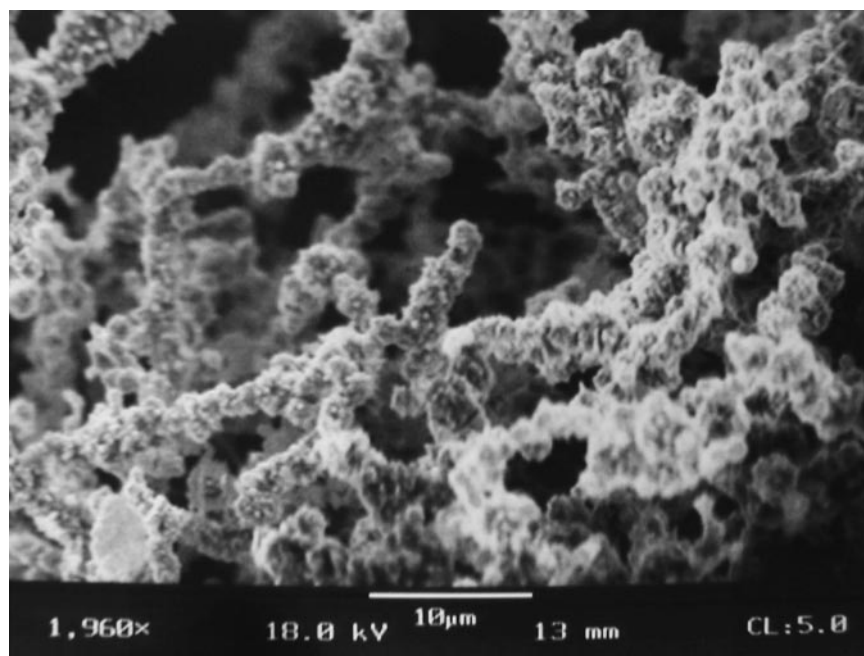

FIG. 3. Scanning electron microscopy photo of nickel catalyst with a morphology of branched filament, 1960× magnification.

atoms present in that molecule were summed. We report selectivities (C_{is}) as the selectivities toward the sum of compounds with specific "i" numbers of carbon atoms.

The compounds analyzed using gas chromatography were as follows: methane, carbon dioxide, carbon monoxide; C_{2s}, ethylene, acetylene, and ethane; C_{3s}, propene, propane, 1,2-propadiene, propyne; C_{4s}, 2-methylpropane, 2-butene, 1-buten-3-yne, 1,2-butadiene, butadiyne, 1-butyne, 2-butyne; C_{5s}, 3-pentene-1-yne; C_{6s}, benzene; C_{7s}, toluene; and C_{8s}, ethylbenzene, ethynylbenzene, and ethenylbenzene.

The conversion in percentage is calculated as follows:

$$X(\%)_{CH4} = (C_T - C_{CH4\ exit})/C_T \times 100, \qquad [1]$$

where C_T is the sum of the concentration of each compound (C_i) multiplied by the number of carbon atoms present in the molecule i (n_i),

$$C_T = \Sigma n_i C_I. \qquad [2]$$

The selectivities in percentage toward compounds with a number of carbon atoms "i" (S_i) were calculated using Eq. [3]:

$$S_i(\%) = (\Sigma n_i C_i)/(C_T - C_{CH4\ exit}) \times 100. \qquad [3]$$

3. RESULTS

Microwave induced-oligomerization of methane was performed at two different frequency levels (2.40 and 4.60 GHz). It was not possible to set the unit to operate under other frequencies. The effect of power and the presence of helium as diluent gas on conversion and product distribution were also studied at these two different frequency values. A summary of the results can be seen in Table 1.

TABLE 1

Results Summary[a]

Feed	Flow rate (ml/min)	Time (min)	Power[b] (W)	Astex unit (2.45 GHz)	Variation Frequency Unit[c] 2.40 GHz	Variation Frequency Unit[c] 4.60 GHz
CH_4	3	3	130	NR	NR	Y
			370	Y	NR	Y
$CH_4 : He$	3 : 9	3	130	NR	NR	Y
			370	Y	Y	Y

[a] NR, no reaction; Y, see Figs. 4–7 for product distribution.
[b] Power levels used: 100, 130, 170, 210, 300, 370 W. Those not shown in the table were neither relevant nor was reaction detected at any frequency.
[c] It was not possible to set other frequency values with successful microwave absorption.

No visible arc formation was detected during these runs and the catalyst bed remained the same after reaction (checked by SEM photographs). Ethylene, acetylene, and ethane were the major C_2 products observed for the oligomerization of methane via microwave heating using Ni powder as a catalyst. Benzene was also formed with selectivities that ranged from 10 to 29%. In the case of 25% diluted methane as a feed and low frequencies (2.45 GHz), low selectivities of benzene were detected (2–5%).

3.1. Pure Methane as Reactant

When using pure methane as reactant, as power increased from 130 to 370 W at 4.60 GHz, conversion increased from 8 to 24%. Selectivities toward C_{2s} decreased from 60 to 45% and selectivities to C_{6s} increased from 6 to 29% (Fig. 4). Acetylene was not detected at low power (130 W). At 370 W, the relative proportions of C_2 products were ethylene > acetylene > ethane. At a low frequency (2.45 GHz), when using pure methane as reactant, oligomerization was not achievable using the variable frequency unit. Therefore, for pure methane, the effect of frequency was compared using an ASTEX unit at the same conditions except at a fixed 2.45 GHz frequency (for more detail see (62)). The selectivities toward C_{2s} decreased from 71 to 45% and the selectivities toward benzene (C_{6s}) increased from 20 to 29% when the frequency was increased from 2.45 to 4.60 GHz at 370 W. The selectivities toward ethylene, acetylene, and ethane decreased as frequency increased, maintaining their relative proportions (Fig. 5).

3.2. Methane Diluted in He (25%)

When the feed was changed to 25% methane in helium, as power was increased from 130 to 370 W at 4.60 GHz, conversion increased from 6 to 8%, selectivities toward C_{2s} decreased from 83 to 72%, and selectivity toward benzene increased from 1 to 10%. Conversion levels were lower than those in the case of using pure methane as a feed (6 and 8% compared to 8 and 24%). Also, while increasing power, changes in selectivity toward C_{2s} and C_{6s} were observed that were less drastic than those when using pure methane (see Figs. 4 and 6).

Acetylene was not detected at 130 W and 4.60-GHz frequency. The relative proportion of C_{2s} changed from ethylene > ethane to ethane > ethylene > acetylene as power was increased from 130 to 370 W (Fig. 6), which was different from the proportion of C_{2s} in the case of pure methane as a feed (ethylene > acetylene > ethane). The systematic effect of frequency was studied using the Lambda variable frequency unit, and comparisons were also made when using the fixed frequency ASTEX unit in order to check for reproducibility of results at low frequency (2.45 GHz).

The data here show that both the ASTEX fixed frequency and the Lambda variable frequency systems behave almost the same when comparing data at low frequency (2.45 GHz)
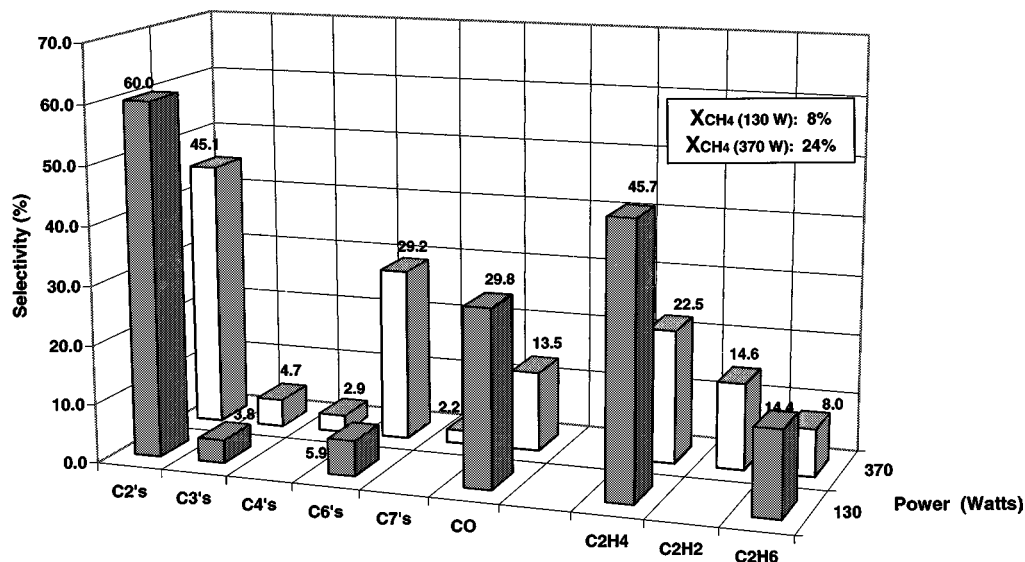
FIG. 4. Effect of applied power on product distribution at 4.60 GHz using pure methane as a feed and nickel powder catalyst.

with respect to conversion levels (about 7%) and product distributions (Fig. 7) at 370 W. As frequency was increased from 2.45 to 4.60 GHz, selectivities toward C_{2s} decreased from 81 to 72% and selectivity toward benzene increased from 5 to 10% (Fig. 7). When using He as diluent at 370 W, the only C_2 detected was ethane at a low frequency value (2.45 GHz). As frequency was increased from 2.45 to 4.60 GHz, the proportion of C_2 products changed from ethane to ethane > ethylene > acetylene (Fig. 7). The effect of frequency on product distribution among C_{2s} was different with respect to the case of pure methane in the feed, as seen in Figs. 5 and 7. The proportion of C_{2s} changed from ethylene > acetylene > ethane to ethane > ethylene > acetylene at 4.60 GHz. At 4.60 GHz and pure methane, se-

lectivity of benzene was higher than that at 4.60 GHz and diluted methane (29 vs 10%, respectively).

There are different sources of oxygen that account for the formation of carbon monoxide and carbon dioxide detected in the products. Nickel catalyst was used as received for the experiments. Subsequent temperature-programmed desorption analysis revealed the presence of oxygenated species in the catalyst, as seen in Fig. 8.

4. DISCUSSION

Microwave radiation does not have sufficient energy to cause any chemical changes, such as breaking bonds and transferring electrons. Nickel catalyst strongly absorbs
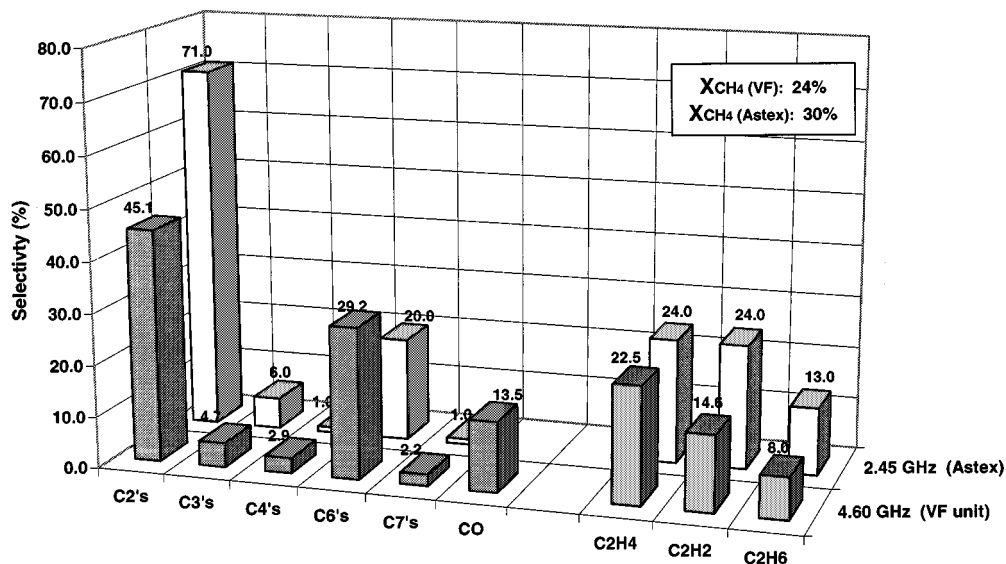

FIG. 5. Frequency effect on product distribution at 370 W using pure methane as a feed and nickel powder catalyst.
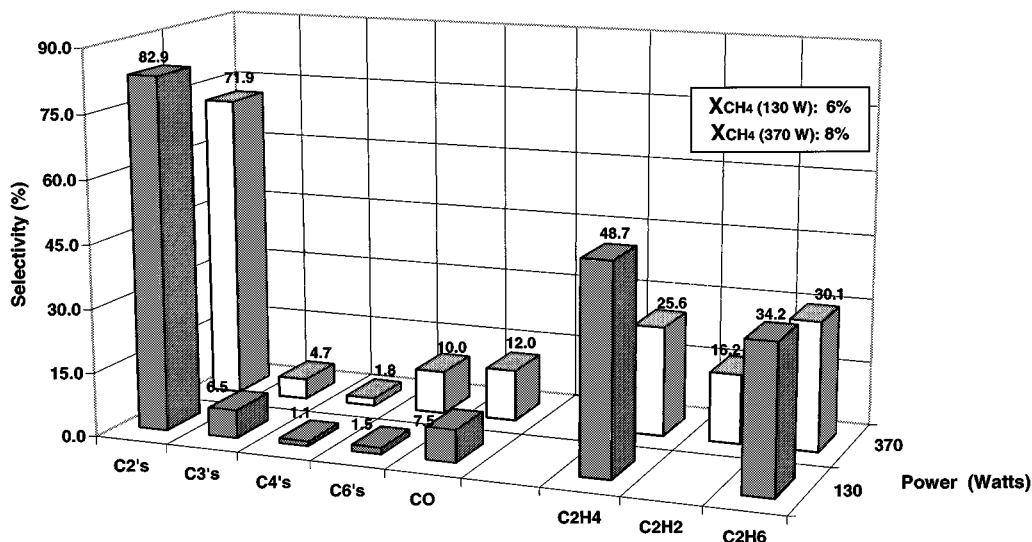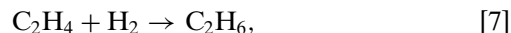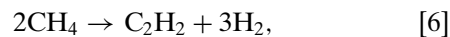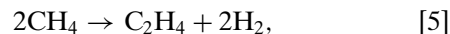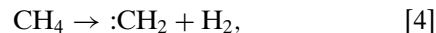
FIG. 6. Effect of applied power on product distribution at 4.60 GHz using methane diluted in helium (25%) and nickel powder catalyst.

microwave energy, providing the necessary kinetic energy for the surface electrons to enhance the surface chemical reaction. The energy absorbed by the metallic sites is transformed from a rapid oscillating electrical field into thermal energy. Since only the catalyst surface site is heated, there is a large temperature gradient between the surface and the bulk of the gas phase. The reaction pathway most likely proceeds via formation of free radical intermediates, as shown by Wan *et al.* (56). The primary decomposition fragment from methane is the methylene radical, which recombines on very hot surfaces to yield acetylene, whereas on cooler surfaces it leads to the formation of ethylene. This finding is in agreement with our results, as seen in Figs. 4 and 6, which

show formation of acetylene as power increased. Some of the proposed reactions are

$$CH_4 \rightarrow :CH_2 + H_2, \qquad [4]$$
$$2CH_4 \rightarrow C_2H_4 + 2H_2, \qquad [5]$$
$$2CH_4 \rightarrow C_2H_2 + 3H_2, \qquad [6]$$
$$C_2H_4 + H_2 \rightarrow C_2H_6, \qquad [7]$$
$$3C_2H_2 \rightarrow C_6H_6. \qquad [8]$$

The presence of H_2 from reaction [4] leads to hydrogenation of olefins and production of ethane, as shown in reaction [7]. The highly reactive methylene ($:CH_2$)
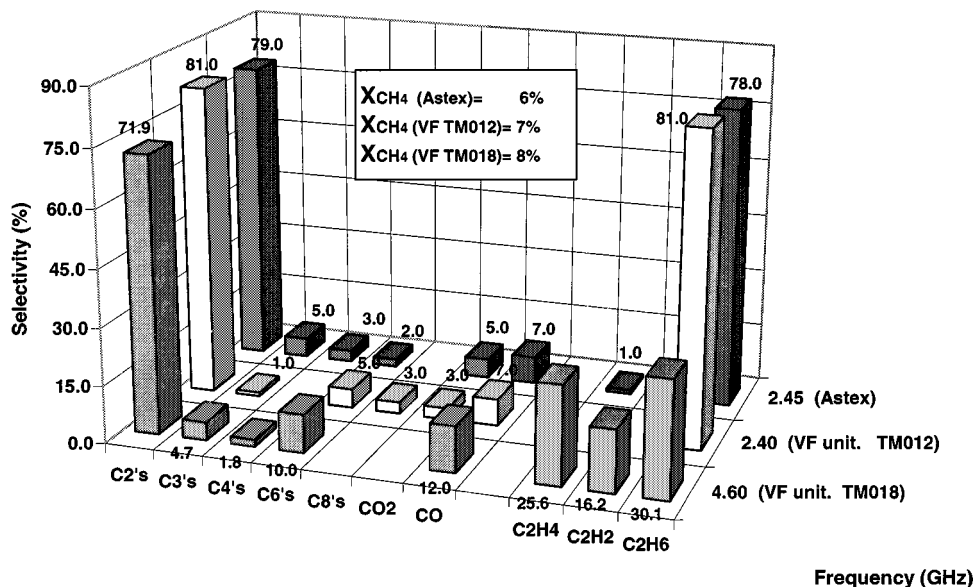

FIG. 7. Frequency effect on product distribution at 370 W using methane diluted in helium (25%) and nickel powder catalyst.
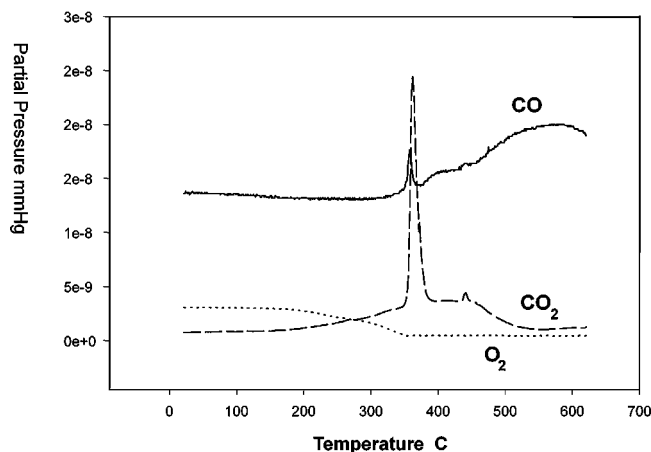
FIG. 8. Fresh nickel catalyst temperature-programmed desorption (TPD)-mass spectrometry (MS) analysis.

intermediate can be used to elucidate the formation of ethylene and acetylene, as indicated in reactions [5] and [6]. The formation of benzene may be explained by the well-known cyclization reaction given in [8]. This is in agreement with the fact that selectivity of benzene increases as selectivity of acetylene also increases. Another viable mechanism for ethylene and acetylene formation could involve the dehydrogenation of secondary hydrocarbons:

$$C_2H_6 \rightarrow C_2H_4 + H_2, \qquad [9]$$

$$C_2H_4 \rightarrow C_2H_2 + H_2. \qquad [10]$$
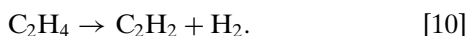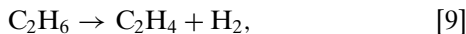
The increase in the duration of the pulse in order to achieve a certain average power and therefore an increase in the surface temperature of the catalyst explains the general trend where conversion increases as power increases. Conversion levels were smaller when using He as a diluent in the feed due to the fact that the residence time was about four times smaller than that when using pure methane in the feed (0.08 vs 0.33 min^{-1}, respectively). Allowing the reactant to spend more time in the reaction zone will permit the methane molecules to find adequate sites for reaction to occur. Since the irradiation time of the catalyst was small (3 min), the bulk temperature was not completely homogeneous. That is, there were hot spots, cold spots, and intermediate temperature spots. Methane will only react on those sites that have reached the proper temperature. Thermodynamic analysis has indicated that a catalyst particle surface temperature on the order of 1400–1600°C is required to yield C_2 products from methane (67). The proportion of C_2 products changed from ethylene > acetylene > ethane when using pure methane to ethylene > ethane > acetylene when using methane and He in the feed. More benzene was also formed when using pure methane. These observable facts can be explained by both the difference in reagent residence time and the difference in con-

centration of methane. Wan found that sudden cooling of products would favor the formation of ethylene and ethane (67). For the case of CH_4 : He feed there is a low concentration of active intermediates and products. Additionally, relatively cold He molecules combined with low residence time would give the molecules more likelihood for rapid quenching. As mentioned previously, benzene very likely comes from the trimerization of acetylene. High concentrations of methane will statistically favor the formation of acetylene and benzene. Including a diluent in the feed will help prevent the coupling of intermediates to these products (63–66).

At present, the issue of microwave effects is very controversial. Unfortunately, many of the expected results from microwave processing, such as rapid and uniform heating, more uniform microstructures, inverse temperature profiles, and selective heating, are included in the general category of microwave effects. However, only those anomalies that cannot be predicted or easily explained based on our present understanding of differences between thermal and microwave heating should be referred to as microwave effects (44, 68). "Microwave-specific" activation has been a debated concept, which actually refers to a unique interaction, reaction, or activation specific to the microwave radiation. Two models of the chemical mechanisms in such reactions have emerged from research work done so far on microwave-induced reaction chemistry. One model assumes that rate enhancement is simply due to thermal dielectric heating and the other assumes that there is a specific activation due to microwave radiation that occurs in addition to the dielectric heating mentioned earlier (69).

Our work is unique in the sense that systematic frequency effects have been found to markedly influence conversion and selectivity under microwave radiation in the oligomerization of methane. The effect of frequency on product distribution for the oligomerization of methane was studied with and without He as a diluent. It is a fact that when increasing microwave frequency, selectivities toward C_{2s} decreased and selectivity toward C_6 increased for both cases (with and without diluent).

All C_2 hydrocarbons decreased as frequency increased when using pure methane feed. When using He as a diluent, ethylene and acetylene increased as frequency increased, while ethane decreased (see Figs. 4 and 7). These effects on product distribution are related to the transverse magnetic modes at different frequencies that would generate diverse transient heating patterns. The two parameters that define the dielectric properties of materials and concomitant heating patterns are dielectric constant and dielectric loss.

As quenching of intermediates has an important role in ethylene formation, different transient heating patterns would affect the environment in which the reaction is taking place, consequently affecting the selectivities of the final

products. The dielectric constant, e', describes the ability of the molecules to be polarized by the electrical field. At low frequencies this value will reach a maximum as the maximum amount of energy that can be stored in the material. As frequency increases, e' decreases, as shown by Mingos and Baghurst (70). The dielectric loss, e'', measures the efficiency at which microwave energy can be converted into heat and goes through a maximum as frequency increases (70). The relationship between these two parameters, e''/e', defines the dielectric loss tangent, $\tan \delta$, which measures the ability of a material to convert electromagnetic energy into heat at a given frequency and temperature. The dielectric loss also goes through a maximum as frequency increases. Therefore, higher formation of benzene–acetylene at higher frequency in our experiments can be explained by the increase in the dielectric loss as frequency increases before going through the maximum. Greater dielectric loss is directly related to greater temperatures and consequently to acetylene formation (56). Acetylene is later consumed in the trimerization reaction to obtain benzene, which is detected in the final products.

5. CONCLUSIONS

Systematic effects of power level, He as diluent, and microwave frequency were studied for the microwave oligomerization of methane using Ni powder catalyst with branched-filament morphology. We are not aware of other heterogeneous catalysis studies where either direct or indirect frequency effects have been observed under microwave radiation. As frequency increased, selectivity toward benzene also increased. When using He as a diluent, as frequency increased, selectivities toward ethylene and acetylene also increased. When pure methane was used, the opposite result was observed. These changes in product distribution are most likely due to different transverse modes that generate different transient heating patterns and changes in dielectric constant and loss of the catalyst.

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