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ARTICLES

Catalytic Oligomerization of Methane via Microwave Heating

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Catalytic microwave heating has been used as a method for the oligomerization of methane to higher hydrocarbons. Many catalysts were tested in this reaction. Nickel powder, iron powder, and activated carbon were the most active and efficient catalysts for the production of higher hydrocarbons. When helium was used as a diluent gas and the applied power was optimized, the selectivities were controlled to the most desired products. Iron powder was active only at high power (1130 W). At these conditions acetylene was avoided and ethylene and ethane were produced in the same proportion. At low power (378 W) with nickel powder as catalyst and no diluent, ethane was the major C_2 hydrocarbon. The amount of acetylene increased when arcing was observed. The proportion of C_2 products changed from ethane > ethylene > acetylene to ethylene > acetylene > ethane when the power was increased from 378 to 1130 W. The major product was CO when high power (1130 W) was used. Selectivities toward C_{3s} and C_{4s} were enhanced to 16 and 18%, respectively, and the major products were propane and methylpropane when He was used as a diluent gas. Activated carbon catalysts and helium diluent led to a product distribution of C_{2s} of ethylene > acetylene > ethane at low applied power (378 W). At medium power (754 W) as time increases, the selectivities to C_{2s} decrease and the selectivity to benzene increases to 33%. Some manganese oxides such as OMS-1, OMS-2, and MnO_2 (dielectric constant, $\epsilon \approx 10^4$) were not active in these reactions. These data suggest that the dielectric constant is not the most important factor in the oligomerization of methane via microwave heating. Conversion and activities of these materials are not proportionally related to the surface area of the catalysts.

I. Introduction

Since methane is relatively inexpensive and there are significant natural gas reserves in the world, of which methane is the major constituent, many studies have been conducted to activate methane to produce valuable products. Many developments have been made in order to activate methane. Some of these studies include the oxidative coupling of methane,[1−4] the conversion of natural gas to liquid fuels,[5] partial oxidation of methane over transition metal oxide catalysts,[6] and the conversion of methane to methanol.[7−10]

The concept of using microwave energy as an activation source for chemical reactions has been studied in the past few years. Since most organic chemicals do not absorb electromagnetic energy in the S-band (2.4 GHz) of the microwave range,[11] it is necessary to use suitable materials that strongly absorb microwave radiation and then efficiently transfer this energy to reactants.

Under ideal conditions and by use of model metallic conductors, charge carriers effectively screen the optical field of the microwave radiation and frequently scatter to produce heat.[11] The efficiency of energy transfer from the microwave absorbing material to the gas phase in a microwave catalytic system depends on several factors[12] such as the nature and configuration of the catalytic sites on the surface, the thermal diffusivity of the catalyst, the power, the way that microwave energy is transferred into the reaction system, and to some degree the frequencies of the electromagnetic waves.[13]

Microwave energy can interact with materials by absorption, reflection, or transmitting energy. Over the past decade microwave heating has been employed extensively in organic[14−18] and inorganic syntheses.[18−32]

The idea of using sensitizers that can absorb microwave energy and transfer heat efficiently in order to selectively activate certain chemical bonds has been used extensively by Wan and co-workers.[33−43] Several applications of high-power microwave catalysis have been demonstrated. These include the synthesis of higher aliphatic and aromatic hydrocarbons from methane, oxidation of hydrocarbons with water as oxidant, the destruction of SO_2 and NO,[33] decomposition of methane,[34,35] catalytic oxidation of ethylene using 1 wt % Pt/Al_2O_3,[36] production of acetylene by microwave catalytic reaction of water and carbon,[37] selective microwave-assisted cracking of benzene to produce acetylene,[38] and acetylene production from the reaction of methane over carbon.[39] Controlled oxidation of methane-doped catalysts irradiated by microwaves,[40] microwave electromagnetic field effects on reforming catalysts,[41] and oxidative coupling of methane over proton conductive catalysts[42] and over rare-earth oxide catalysts[43] have been studied.

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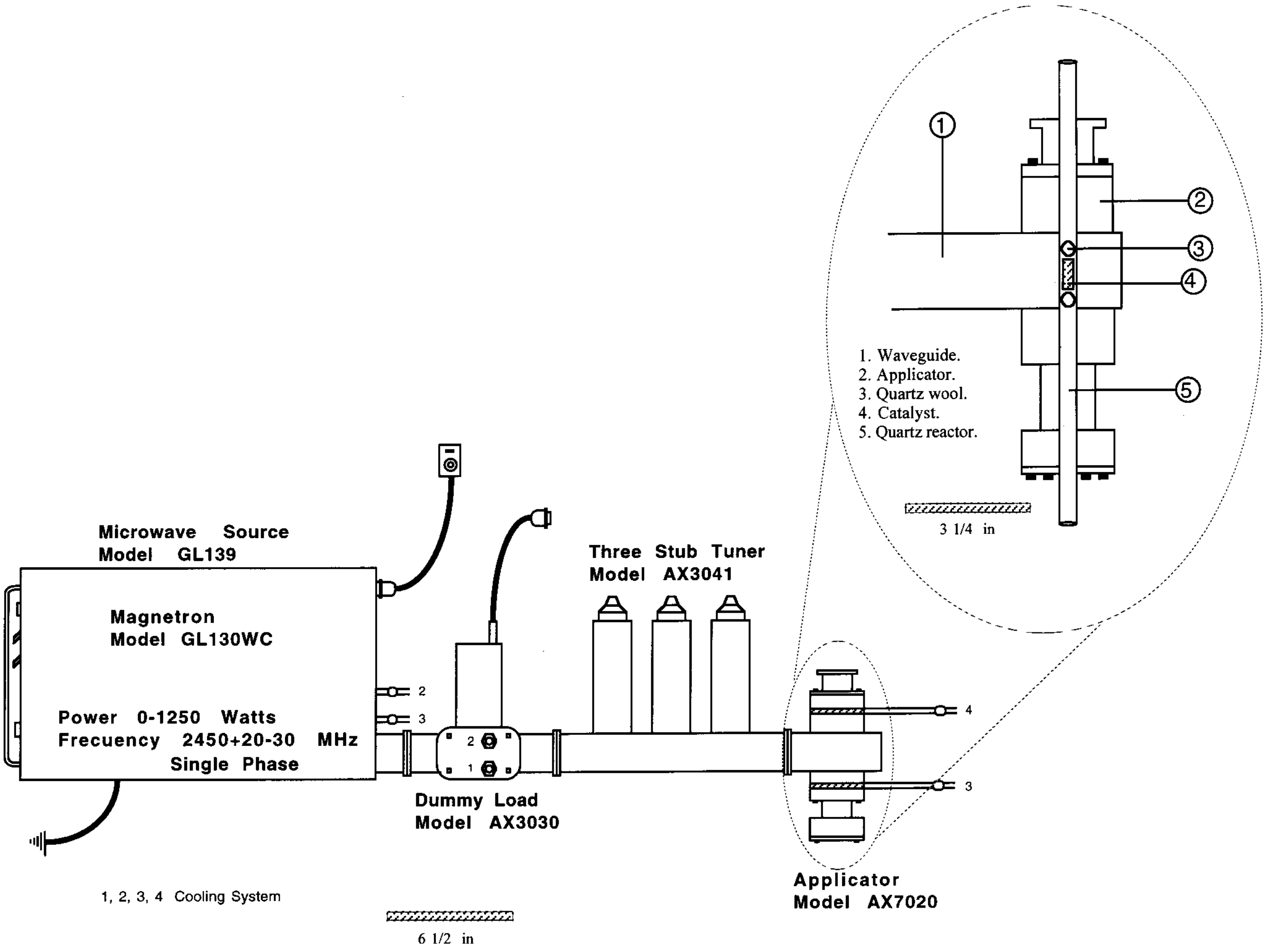
CHART 1: Microwave Apparatus, Applicator, and Reactor



Although many processes have been developed for the conversion of methane to higher hydrocarbons, it is not yet clear how microwave pulses or continuous microwave heating induces oligomerization. In this paper, we studied effects of different catalysts, applied microwave power, and the presence of helium as diluent on the conversion and product distribution of methane oligomerization induced via microwave heating.

II. Experimental Section

A. Microwave Apparatus and Gas System. Microwave-induced oligomerization (MIO) of methane to higher hydrocarbons was carried out in a straight $^3/_8$ in. quartz reactor, which was mounted vertically inside the applicator of the microwave apparatus as shown in Chart 1. An ASTEX microwave power source model GL139 with a magnetron type GL 130WC, a three-stub tuner model AX3041, and an ASTEX applicator model AX7020 were used for these experiments. This power supply provided up to 1250 W of power at an operating frequency of 2.54 GHz. The power was emitted in pulses with a periodicity of 8.3 ms (120 Hz).

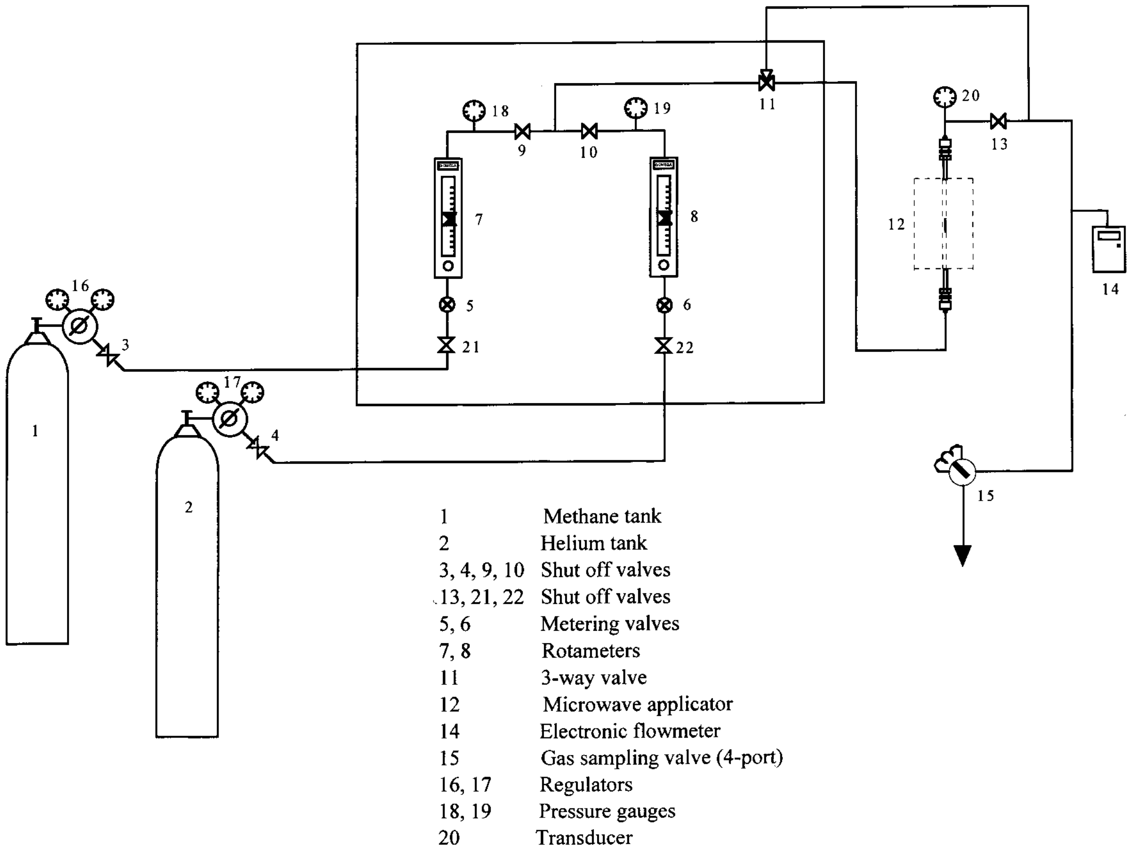
To achieve a desired average power, the pulse duration or the pulse width and the amplitude were changed. Thus, varying the power exposure of the catalyst by varying the emitted power from the source essentially results in different duty cycles at different power levels.

The oligomerization reactions were run under a continuous flow. Gases were mixed on line using a panel as shown in Chart 2 when necessary. High Purity (HP) grade methane obtained from Matheson and Ultra High Purity (UHP) helium purchased from Airgas were used. An electronic J&W Scientific gas flow meter was utilized to measure the flow rate of the gases, and a set of rotameters (Omega FL-3545-HRV and FL-3541-HRV series) coupled with fine metering valves were used to control the flow rates.

B. Catalysts or Dielectric Materials. Several different materials were tested as catalysts for the oligomerization of methane, including some manganese oxide materials. Most of the materials were purchased from different companies (see Table 1 for more information), and they were used as received. In Table 1, the literature values of the dielectric constants for each material in reference to a vacuum and the temperature and the frequency at which they were measured are given.[44] Synthetic todorokite [an octahedral molecular sieve (OMS) designated as OMS-1 having a 6.9 Å pore size] and synthetic cryptomelane [(a K^+ hollandite) another OMS structure having a 4.6 Å pore size, which is designated as OMS-2 made by conventional methods[45−48] doped with nickel and cobalt] were tested as catalysts for methane oligomerization.

Approximately 0.1 g of catalyst was placed inside the quartz reactor, which was plugged at both ends with high-purity quartz wool. The catalyst was placed in the quartz reactor, which was inside the applicator so that the material was positioned at the center of the waveguide cavity (see the expanded portion of Chart 2). To purge the atmosphere, helium gas flowed through the reactor for 30 min prior to starting the microwave absorption.

CHART 2: Gas System



1	Methane tank
2	Helium tank
3, 4, 9, 10	Shut off valves
13, 21, 22	Shut off valves
5, 6	Metering valves
7, 8	Rotameters
11	3-way valve
12	Microwave applicator
14	Electronic flowmeter
15	Gas sampling valve (4-port)
16, 17	Regulators
18, 19	Pressure gauges
20	Transducer

TABLE 1: Information about Dielectric Materials

material	source	dielectric constant[30,a]	*T* (K)	*v* (Hz)
MnO_2	Diamond Shamrock Chemicals	10 000	298	10^4
TiO_2	Fisher Scientific	170	300	10^4-10^6
SnO_2	Mallinckrodt Chemical Works	14	298	10^4-10^{10}
Si	Atlantic Equipment Co.	12.1	4.2	10^7-10^9
CaO	Baker and Adanson	11.8	283	2×10^6
SiC	Aldrich	9.72	298	$10^{12}-10^{14}$
SiO_2	Silica gel, Davisil Aldrich	4.6	298	9.4×10^{10}
Sm_2O_3	American Potash & Chemical Co.		*b*	*b*
Pt/Al_2O_3 (0.2 wt %)	Alfa Products	*b*	*b*	*b*
C_{60}	Aldrich	*b*	*b*	*b*
Co	Inco Co.	*b*	*b*	*b*
Fe	Inco Co.	*b*	*b*	*b*
Ni	Inco Co.	*b*	*b*	*b*
activated carbon[c]		*b*	*b*	*b*
OMS-1-Ni (1%)	Synthesized at Uconn[54−56]	*b*	*b*	*b*
OMS-2-Ni (0.1%)	Synthesized at Uconn[54−56]	*b*	*b*	*b*
OMS−Co (1%)	Synthesized at Uconn[54−56]	*b*	*b*	*b*

[a] Referred to vacuum. [b] Not available. [c] 2200 and 3100 m^2/g.

Temperature measurements of the catalyst bed were made using a microprocessor thermometer model HH21 with a type K thermocouple purchased from Omega. The temperature was not measured in situ, since the thermocouple will interfere with the microwave field. Therefore, after we achieved steady state under reaction conditions, we shut off the microwave power and rapidly inserted the thermocouple in the catalyst bed to obtain information about the temperatures reached at different applied power levels for the different materials used as catalysts.

The conditions at which these experiments were run include a 3−5 mL/min flow rate of methane, a 1−10 mL/min flow rate of helium, and atmospheric pressure. Catalyst activities were tested at maximum power using 3 mL/min of methane and 9 mL/min of helium. For those catalysts that were active, runs were made at low, medium, and high power and analyses were performed at different sampling times (from 1 to 30 min).

C. Product Analysis. Products were trapped with a gas sampling valve (15) and analyzed by connecting it between a helium tank and an HP5890 series II chromatograph, which was equipped with a mass detector. The GC has a sampling valve and another six-port valve for column switching. Three analytical columns were used for the separation. A precolumn (HP Porapack Q, $^1/_8$ in. × 6 ft) was used to separate the permanent gases from the rest of the sample. The permanent gases are further separated individually on a molecular sieve column (HP Molsieve, 25 m × 0.53 mm × 50 mm), while the rest of the sample mixture is back-flushed from the precolumn and passed

TABLE 2: Conditions at Which Oligomerization of Methane Was Performed

						comments			
series	catalyst[a]	m_{CH4} (mL/min)	m_{He} (mL/min)	power (W)	t (min)	AF[b]	CF[b]	MP[b]	other
A	Ni	3	0	378−755−1130	3	Y[1130]	N	Y(p[c])	on/off[d]
B	Ni	3	0	378−755−1130	3	N	N	N	on/off
C	Ni	3	0	378−755−1130	2, 3, 20	N	Y[378(20)]	N	same load as B
D	Ni	3	0	315−378−503−628−754−1130	1, 10, 20, 30	N	Y[503]	N	
E	Ni	3	0	378−755−1130	3, 20	Y[1130(3)]	Y	Y[1130]	
F	Ni	3	9	378−503−628−754−1130	1, 10, 30	Y[1130]	Y	Y[1130]	
I	AC-1[e]	3	9	315−378−754−1130	1, 10, 20	Y[315(20)]	Y[315(20)]	Y[754(20)]	
J	AC-2	3	9	315−378−754−1130	1, 10, 20	N	Y[315(20)]	Y[754]	
K	AC-1	3	0	190−378−754−1130	3, 10, 20	Y[754(3)]	Y	Y[754(20)]	
L	Fe	3	0	378−755−1130	3, 20	N	N	N	

[a] 100 mg of catalyst was used as received. [b] AF = arc formation; CF = coke formation; MP = melting process; N = no; $Y[x(y)]$ = yes, x = power (W) at which phenomenon occurs, y = time (min) at which phenomenon occurrs. [c] p = partially. [d] On/off = unit was turned off after sample was taken at specific average power value. [e] AC-no. = activated carbon; no. = 1 (2200 m^2/g), 2 (3100 m^2/g).

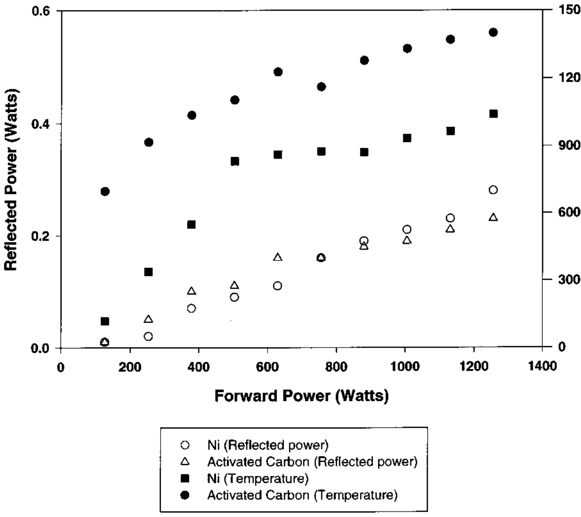


Figure 1. Reflected power vs applied power and effect of applied power on temperature.

through a split to a Poraplot Q column (HP Poraplot Q, 25 m × 0.32 mm). The splitting ratio is typically 30:1. The permanent gases, after passing through the Molsieve column, re-enter the precolumn and then enter the split and the Poraplot Q column.

The total conversion of methane was estimated with a carbon balance. All the compounds multiplied by the number of carbons present in that molecule were summed. We report selectivities as the selectivities toward the sum of the compounds with specific "i" numbers of carbon atoms (C_{is}).

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

The conversion in percentage is calculated as

$$X(\%)_{CH4} = \frac{C_T - C_{CH4exit}}{C_T} \times 100$$

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

$$C_T = \sum n_i C_i$$

The selectivities in percentage toward compounds with number of carbons "i" (S_i) were calculated using

$$S_i(\%) = \frac{\sum n_i C_i}{C_T - C_{CH4exit}} \times 100$$

III. Results

A. General Observations. Oligomerization of methane to higher hydrocarbons was performed by means of catalytic microwave heating in a controlled manner. Microwaves were coupled to the catalyst bed, and reflected power was minimized using the three-stub tuner of the microwave system (Chart 1). The reflected power was measured at different applied powers for all the catalytic materials we used, and the values for nickel and activated carbon are shown in Figure 1. The reflected power was found to be very low with respect to the applied power (less than 0.03%). When arcing was formed, the reflected power was increased instantaneously up to 0.06%, which is still very low in comparison with the applied power.

The temperatures reached in the bulk of the catalyst bed as a function of the applied power for nickel and activated carbon (3100 m^2/g) are shown in Figure 1. Activated carbon absorbs microwave energy more efficiently than nickel, which results in much higher temperatures for carbon than for nickel at the same applied power. Very high temperatures were observed (up to 1250 °C), and in some cases the quartz reactor melted. These data suggest that temperatures reached in the reactor were higher than the ones detected with the thermocouple.

Different materials were tested as catalysts for the oligomerization of methane (Table 1). Results suggest that other systems such as activated carbon, nickel, and iron powder were considerably more active than manganese oxide materials. All other catalysts were not at all active for this reaction under these experimental conditions.

The parameters of all experiments, such as catalyst, flow rates of methane and helium, applied average power, sampling time, and relevant comments regarding the reaction, are shown in Table 2.

Typical product distributions consist of ethane, ethylene, and acetylene for C_{2s}, propane, propene for C_{3s}; methylpropane, benzene, and C_{8s} were also detected. The major products were the C_{2s}. Selectivities toward different products were controllable by changing and optimizing the reaction conditions and the catalyst that was used.

In some cases arc formation was observed accompanied by minor explosions. Catalysts that have produced discharges in the microwave field could not be heated again without the

TABLE 3: Most Relevant Results for the Oligomerization of Methane via Microwave Heating

						selectivities (%)									C2's selectivities (%)		
run	power (W)	sample	CH_4/He	time (min)	conversion (%)	C2	C3	C4	C5	C6	C7	C8	CO_2	CO	ethylene	acetylene	ethane
series A	754	Ni	3/0	3.0	36.7	56.2	2.3	0.0	0.0	0.1	0.0	0.0	1.5	39.8	15.3	38.4	2.5
series B	1130	Ni	3/0	3.0	21.5	84.2	1.6	0.0	0.0	0.0	0.0	0.0	0.2	13.8	45.5	31.4	7.3
series D	503	Ni	3/0	30.0	48.2	84.9	0.8	0.9	0.1	0.9	0.0	0.0	0.1	12.4	24.3	59.1	1.5
	628	Ni	3/0	10.0	10.0	18.3	5.3	0.0	0.0	4.3	0.0	0.0	5.5	66.7	0.0	0.0	18.3
	1130	Ni	3/0	1.0	22.4	12.0	0.5	0.2	0.2	24.5	1.0	0.3	0.1	61.2	10.2	0.8	1.0
	1130	Ni	3/0	10.0	19.7	11.9	0.5	0.0	0.0	5.2	0.3	0.1	0.1	81.8	10.7	0.9	0.4
series E	378	Ni	3/0	20.0	35.5	70.6	6.3	1.2	0.6	20.0	0.9	0.4	0.0	0.0	34.3	33.6	2.7
	754	Ni	3/0	20.0	50.0	76.8	1.2	0.6	0.3	10.2	0.2	0.0	0.0	10.7	36.4	38.4	2.0
series F	503	Ni	3/9	10.0	7.0	55.0	16.3	18.0	0.0	1.2	1.0	2.7	5.8	0.0	0.0	0.0	55.0
	628	Ni	3/9	1.0	10.1	46.8	9.1	7.3	0.5	1.8	1.6	0.8	9.7	22.3	6.6	3.1	37.1
	754	Ni	3/9	1.0	4.0	69.9	8.0	4.9	0.0	0.4	0.3	1.3	3.8	11.3	5.2	2.3	62.5
	1130	Ni	3/9	1.0	45.2	36.6	3.6	1.4	0.1	0.6	0.1	0.0	0.7	57.0	18.9	3.2	14.4
series I	378	AC-1	3/9	10.0	24.3	47.7	0.8	0.0	0.1	0.0	0.0	0.2	0.2	51.0	37.8	7.1	2.8
	378	AC-1	3/9	20.0	14.1	65.6	1.5	0.5	0.2	28.4	0.0	0.0	0.2	3.7	48.5	11.0	6.1
series J	378	AC-2	3/9	20.0	19.5	94.6	1.5	0.1	0.0	0.1	0.0	0.0	0.1	3.6	66.5	19.5	8.6
	754	AC-2	3/9	1.0	7.5	55.7	18.7	0.4	0.0	0.4	0.0	0.1	0.5	24.2	33.6	16.0	6.1
series K[a]	378	AC-1	3/0	20.0	13.4	89.1	6.5	0.2	0.0	0.0	0.0	0.1	0.2	3.9	67.9	7.9	13.4
	565	AC-1	3/0	3.0	19.5	91.4	4.1	0.1	0.0	0.3	0.0	0.0	0.8	3.3	71.1	7.7	12.6
	565	AC-1	3/0	10.0	14.7	92.2	4.8	0.6	0.1	0.3	0.0	0.2	0.2	1.6	72.5	7.5	12.2
	565	AC-1	3/0	20.0	14.6	82.4	6.0	0.5	0.3	8.9	0.0	0.1	0.1	1.7	63.2	8.3	10.9
	754	AC-1	3/0	3.0	25.6	85.2	3.1	0.1	0.0	8.8	0.0	0.0	0.6	2.1	61.2	11.9	12.2
	754	AC-1	3/0	10.0	12.6	72.9	2.8	0.4	0.3	20.1	0.0	0.1	0.2	3.2	57.0	7.2	8.7
	754	AC-1	3/0	20.0	16.3	60.1	3.7	0.4	0.1	33.4	0.0	0.0	0.1	2.0	49.3	3.5	7.3
series L	1130	Fe	3/0	3.0	11.0	21.0	1.0	0.4	0.1	0.0	0.0	0.0	35.0	42.0	9.0	0.0	12.0

[a] Purging all O_2 at low power. 100 mg.

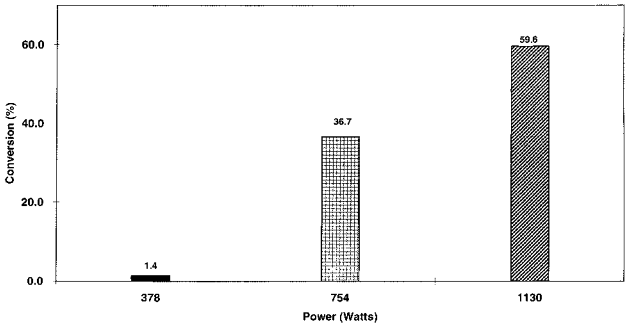


Figure 2. Effect of applied power on conversion using nickel powder (conditions: series A).

production of discharges. Catalysts may undergo a change in dielectric properties upon heating in the microwave field, and this may dramatically alter their ability to interact with the applied field.[43] Usually, the nickel was melted if arcing was present during reaction. Iron did not form arcs or melt during the oligomerization of methane. Coke was deposited on the walls of the quartz reactor in most cases. Coke was not present for iron and nickel at very short reaction times. Activated carbon glowed at very low power (190 W), and it formed a carbon-like coating on the walls of the reactor at the end of the reaction. In Table 3 we show the most relevant results obtained for the oligomerization of methane via microwave heating using nickel powder, activated carbon, and iron powder as catalysts. The details for these runs will be discussed in the following sections.

B. Nickel Powder. For nickel powder runs were made with and without helium as diluent at different power levels, which are in most cases 378, 755, and 1130 W. A plot of conversion versus power is shown in Figure 2. In general, conversion increases as applied power increases. In some cases, when the same catalyst bed was used for long periods of time at different power levels, the contrary was observed, suggesting catalyst deactivation.

When the run was carried out without diluent and a period of 3 min was used, the observed products were carbon monoxide, carbon dioxide, and C_2 hydrocarbons (Figure 4).

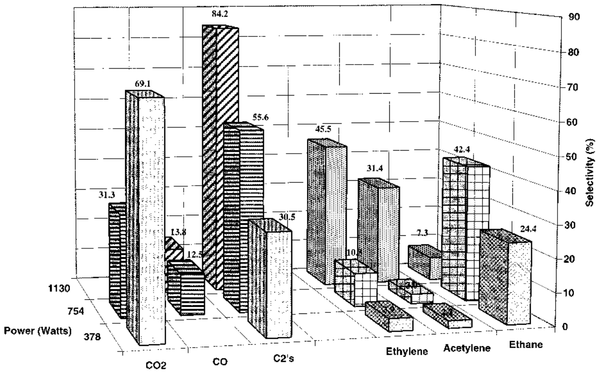


Figure 3. Selectivity vs applied power and effect of applied power on product distribution of C_{2s} using nickel powder (conditions: series B).

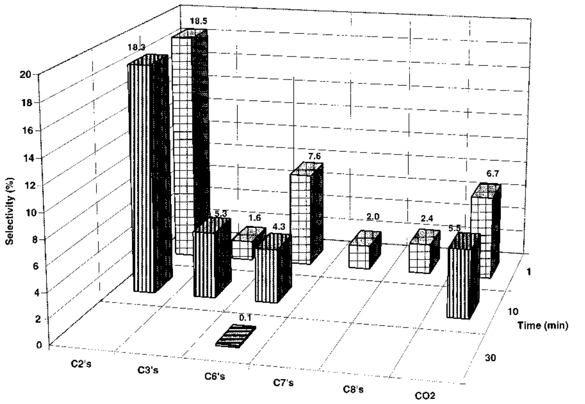


Figure 4. Selectivities vs time at 628 W using nickel powder (conditions: series D).

Selectivity toward C_{2s} increases as applied power increases unless arc formation occurs, which promoted formation of acetylene (C_2H_2) and carbon monoxide (Figure 3). At low power (power $\leq$ 378 W) with no diluent, the major product among the C_{2s} was ethane (C_2H_6). When arc formation is noticeable at 503 W, the proportion of C_2 products changed from ethane >

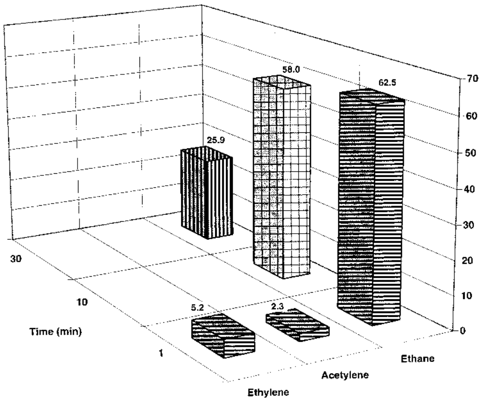


Figure 5. Product distribution of C_{2s} vs time at 754 W using nickel powder (conditions: series F).

ethylene > acetylene to ethylene > acetylene > ethane. At high power (1130 W) the amount of C_2H_2 increases (Figure 3).

When the reaction was run for longer times (≥30 min), the general tendencies remained the same. Conversion and selectivity values were not reproducible possibly because of changes in the catalyst due to arcing. When arcs were not observed (series C), as time increases from 2 to 20 min at 378 W, total conversion and selectivities toward C_{2s} hydrocarbon decrease from 54 to 13% and selectivities toward CO increase from 44 to 85%. At 378 and 755 W the selectivities toward C_{2s} were ethylene (28%) > acetylene (21%) > ethane (5%) at 378 W and 2 min of reaction. At very high power (1130 W) the methane was converted to CO ($S_{CO} = 99\%$). At low power (315−378 W) with no diluent, although conversions were very low (~2%), the oligomerization of methane to hydrocarbons ranged from carbon compounds with one carbon atom (CO and CO_2) up to compounds with eight carbon atoms. Selectivities toward CO_2 were higher than selectivities toward CO during the reaction (15% vs less than 1% at 315 W and 10 min of reaction). Under these conditions the major product of the C_{2s} is ethane ($S_{ethane} = 73\%$, $S_{ethylene}$ and $S_{acetylene} \approx 1\%$ at 315 W and 10 min of reaction).

With pure methane feeds, although the major product is CO (not shown in Figure 4), the selectivities to C_{3s} can be as high as 5% at 628 W (Figure 4). The selectivity toward benzene (C_6H_6) can be as high as 25% at 1130 W. The selectivities toward benzene can be as high as 20% and 10% at 378 and 755 W, respectively, when arcing is observed.

The selectivity toward C_2 hydrocarbons increased as power increased when a ratio of methane/helium of 1:3 was used. After 10 min at any power setting the only C_2 present is ethane (Figure 5). At low power (378 W), the selectivities to C_{3s} were as high as 18% when helium is used as a diluent. The selectivities toward C_{3s} and C_{4s} were as high as 16 and 18%, respectively, when the power is increased to 503 W (Figure 6). The major product among the C_{3s} was propane and for the C_{4s} was methylpropane.

C. Activated Carbon. When the catalyst is changed to activated carbon, the conversion again increases as the applied power increases. High power levels (greater than 754 W) lead to conversions of almost 100% (Figure 7). At high power (1130 W) with helium diluent the only product is CO ($S_{CO} = 100\%$). At low power (between 315 and 378 W) when times on stream are enhanced (from 1 to 20 min), the selectivities toward C_{2s} and to CO increase (Figure 8). In this case, selectivities of ethylene are greater than ethane and no acetylene is formed. When the power is increased to 378 W, acetylene is generated and the selectivities are in the order ethylene > acetylene > ethane (49, 11, and 6%, respectively, at 20 min of reaction). The major C_3 hydrocarbon product is propene.

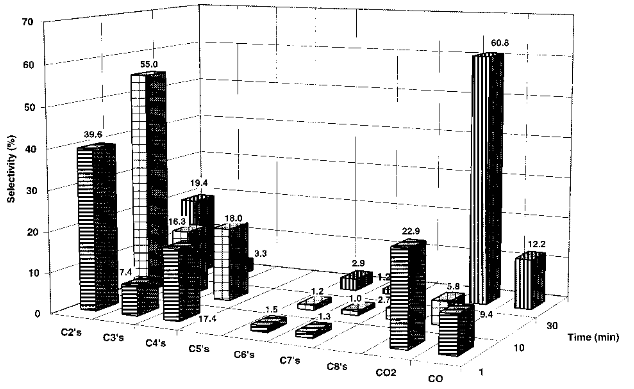


Figure 6. Selectivities vs time at 503 W using nickel powder (conditions: series F).

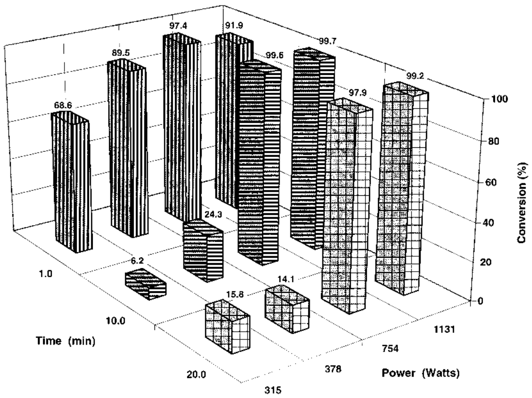


Figure 7. Applied power and time of reaction effect on conversion (conditions: series I).

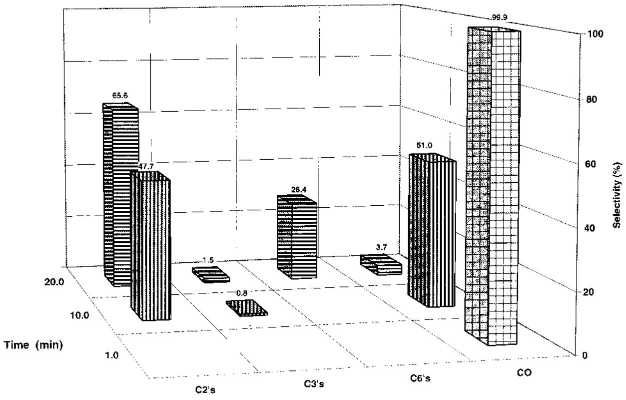


Figure 8. Product distribution vs time at 378 W using AC-1 (conditions: series I).

When no diluent is used at very low power (190 W), conversions are very low, around 7%. As time on stream increases (from 15 to 85 min), the selectivities toward C_{2s} increase from 30 to 88% and selectivity toward CO decreases from 62 to 7%. No acetylene is formed during these conditions, and the selectivity toward ethylene is greater than that of ethane. At an intermediate power of 378 W, as time increases from 3 to 20 min, selectivities to CO decrease to 4% and C_{2s} and C_{3s} increase to 90 and 6%, respectively. Propene is again the major C_3 product detected. The amount of C_2 product decreases when the power is increased to 754 W; as time increases, the selectivity toward C_{6s} increases to 33% (Figure 9). The selectivities of C_{2s} change to ethylene > ethane > acetylene

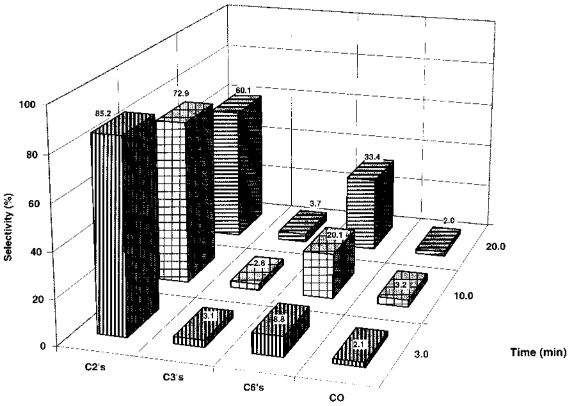


Figure 9. Product distribution vs time at 754 W using AC-1 (conditions: series K).

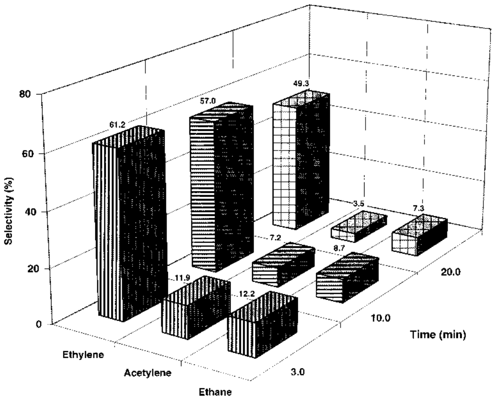


Figure 10. Product distribution of C_{2s} vs time at 754 W using AC-1 (conditions: series K).

(Figure 10) when medium (566 W) and high power (754 W) levels are used.

D. Iron Powder. Iron powder was active at high power values (1130 W). The conversion decreases from 10 to 3% as time increases from 3 to 20 min. Selectivity to CO was enhanced to 70% at high power (1130 W) and longer times (20 min). Selectivity to C_2 hydrocarbons decreases from 21 to 12% as time increases from 3 to 20 min. No acetylene was produced during reaction. Ethane was the major product among the C_{2s}. Ethylene was also produced only at 3 min of reaction.

IV. Discussion

A. General Comments and Mechanistic Ideas. Minimization of the reflected power was achieved by proper use of the three-stub tuner; therefore, most of the applied power was delivered to the catalytic bed. To achieve an average desired power, the pulse duration in these experiments also changed. The pulse width and amplitude are increased as the average power increases. This might explain the trend of increased applied power with an increase in the bulk measured temperature. Since temperatures could not be measured in situ, the ex situ measurements appear to be much lower than real temperatures on the basis of physical evidence of melting or fusing processes of nickel catalysts and the quartz reactor. Ethylene, ethane, and acetylene were the major C_2 products for the oligomerization of methane via microwave heating using nickel powder, activated carbon, and iron powder as catalytic materials.

Reaction mechanisms that account for the detected C_2 products have been proposed by other authors.[33−35,37,39] Equations 1−6 summarize some of the proposed reactions:

$$CH_4 \rightarrow :CH_2 + H_2 \qquad (1)$$

$$2CH_4 \rightarrow C_2H_4 + 2H_2 \qquad (2)$$

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \qquad (3)$$

$$C_2H_4 + H_2 \rightarrow C_2H_6 \qquad (4)$$

The presence of H_2 from reaction 1 leads to hydrogenation of olefins and production of ethane as shown in reaction 4.

Another viable mechanism for ethylene and acetylene formation could involve the dehydrogenation of secondary hydrocarbons:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad (5)$$

$$C_2H_4 \rightarrow C_2H_2 + H_2 \qquad (6)$$

The reaction paths most likely proceed via formation of free radical intermediates. The formation of propane, propene, and benzene may be explained by reactions given in eqs 7−9:

$$C_2H_6 + CH_2 \rightarrow C_2H_8 \qquad (7)$$

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad (8)$$

$$3C_2H_2 \rightarrow C_6H_6 \qquad (9)$$

The mechanism by which C_{4s} to C_{8s} are formed could be very complicated, and many different pathways could be involved for the production of these compounds.

Metal samples or continuous metal films in high microwave fields result in large electric field gradients and may cause visible and at times dramatic electric discharges.[49] Arcs are short-lived, localized plasmas caused by the build-up of an intense electrical field. The electrical field attempts to remain continuous throughout the volume of the cavity but will be zero at the metal surface. Arcs are ionized gas, which can be destructive to the metal surfaces at which they form. Once an arc occurs and damages a surface, the tendency is for that surface to more easily produce more arcs. The effect of an arc on a reaction depends strongly on the reaction itself. High-energy excited-state atoms, ions, or molecules produced during arc formation can lead to explosions. Variable frequency applicators can eliminate the arcing problems experienced in microwaves ovens when a metal or a semiconducting material is irradiated.[50]

B. Catalyst, Applied Power, and Diluent Effects on Product Distribution. Ni powder, activated carbon, and iron powder are active catalysts for the oligomerization of methane. Our results for Ni are in agreement with studies by Wan and co-workers.[11,33,37,51−52] Conversion increases as power increases, and this trend might be explained by the increase in the duration of the pulse in order to achieve a certain average power and therefore an increase in the bulk temperature of the catalyst. There is evidence that the catalysts are changing during reaction when conversion decreases as time and power increase.

The presence of CO_2 and CO as products could come from oxygen adsorbed on the nickel, nickel oxide (since we did not reduced the nickel before reaction), as well as from sputtering of the walls of the reactor. The results from activated carbon are novel and difficult to compare to data for nickel and iron powders. One reason for this difficult comparison is that the surface area of the activated carbon samples is as high as 3100 m^2/g whereas the nickel and iron powder are considerably smaller, on the order of 230 m^2/g.

The most fascinating data are for nickel and activated carbon systems. By use of nickel as a catalyst and with no diluent, selectivity to benzene was 24%. The proportions of ethylene, acetylene, and ethane could be controlled depending on the conditions used. Acetylene increases when arcing is present and is in accord with data for oligomerization of methane via microwave plasmas.[53] The selectivities are highly dependent on the nature and concentration of diluents such as helium and the average applied power. Oligomer products such as C_{3s} and C_{4s} were enhanced up to 16 and 18%, respectively, when helium is used as a diluent for the nickel system and at medium power (503 W). The diluent effect may be due to partial absorption of microwave energy by the helium atoms and collisional interactions of such species with methane molecules.

When activated carbon was used as a catalyst, the overall selectivity to benzene can be as high as 33%. Selectivities to ethane and ethylene were reached at high power (1130 W) with no production of acetylene when using iron powder as catalyst.

Nickel, iron powder, and activated carbon are the most active catalytic materials for the oligomerization of methane using microwave heating. Manganese oxide systems such as OMS-1, OMS-2, and OL-1 are not very active for this reaction. The dielectric constant of manganese oxide is on the order of 10 000; i.e., one of the highest values reported for any material. The data reported here clearly show that dielectric constants are not the most important parameters in the catalytic oligomerization of methane induced via microwave heating.

The surface area of activated carbon is 2 orders of magnitude larger than the surface area of Ni powder. The data reported here also show that conversion and activity of these materials are not proportionally related to the surface area of the catalysts we used. One possible explanation for the lack of direct relationship between surface area and conversion might be the effect of the interaction of microwaves with surface functional groups such as OH groups and other catalytic intermediates like CH_3, CH_2, CH, and other species. Such functional groups may also influence the adsorption of the reactant species.

V. Conclusions

The microwave heating oligomerization experiments have shown that nickel, iron powder, and activated carbon can act as selective catalysts for oligomerized products of methane. Oligomers ranging from C_2 to C_6 hydrocarbons (benzene) have been prepared in good selectivity depending on the nature of diluent and the power levels used in the microwave reactor. The use of He as diluent gas favors the oligomerization of methane via microwave heating. When He is used as a diluent and Ni powder as a catalyst, selectivities toward C_{3s} and C_{4s} were enhanced up to 16 and 18%, respectively. Although He might be expensive, it is an additional parameter that should be considered. Selectivities toward benzene as high as 33% were achieved by using activated carbon as a catalyst. Further optimization of parameters that can influence and maximize the product distribution toward desired products for the oligomerization of methane is in progress and will be reported later.

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