ACADEMIC PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 218 (2003) 201–208

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Oligomerization of methane via microwave heating using Raney nickel catalyst

L. Daniel Conde,[a] Carolina Marún,[b] and Steven L. Suib [a,b,c,*]

[a] *Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3060, USA*
[b] *Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269-3060, USA*
[c] *Department of Chemistry, Department of Chemical Engineering, and Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3060, USA*

Received 25 November 2002; revised 25 February 2003; accepted 25 February 2003

Abstract

Raney nickel has been used for the catalytic activation of methane using microwave radiation as a heating source. The effects of irradiation time, power level, and pretreatment of the catalyst have been studied. Compared to previous studies, higher catalytic activity was observed for Raney nickel than for regular nickel powder. The maximum conversion obtained was 24% at 400 W and 10 min of irradiation time. For regular nickel powder that conversion can be achieved only after 700 W of power and more than 20 min of reaction. BET surface area, scanning electron microscopy, X-ray photoelectron spectroscopy, and temperature-programmed desorption and reduction analysis were performed to characterize the catalyst before and after reaction. Oligomers such as ethylene, benzene, and ethane have been prepared selectively under different conditions. Ethylene, with a selectivity of 70%, was the major product at 530 W and 5 min of irradiation time. Deactivation of Raney nickel by fouling and sintering was observed after 500 W and/or 15 min of reaction.

Keywords: Microwave catalysis; Microwave frequency effects; Activation of methane; Methane oligomerization

1. Introduction

Natural gas is essentially methane (83–97 vol% depending on the origin) and therefore difficult to liquefy and quite chemically unreactive. Methane is thermodynamically stable with respect to its elements. The reactions to make other hydrocarbons, all of which are less stable than methane around 1000 °C, have unfavorable free energies of reaction and are strongly limited by equilibrium. Such reactions need a considerable energy input, and therefore temperatures above 1000 °C are required to transform CH_4 into benzene, acetylene, ethylene, and ethane. Methane is a very valuable fuel from the environmental point of view and the production of energy is so far its main use. However, a more rational use of methane is that it should also be used to make either petrochemical or gasoline components.

Many efforts have been focused on the activation of methane to more valuable products in the last two decades [1–3]. Thermal [4,5], homogeneous [6,7], and heterogeneous [8,9] catalytic conversion of methane to higher hydrocarbons has been studied by many authors. The idea of using sensitizers that can absorb microwave energy and transfer heat efficiently in order to selectively activate C–H bonds from methane has been used extensively by Wan and coworkers [1,2,10] and Chen et al. [3].

In a previous work, we had studied the oligomerization of methane to higher hydrocarbons using Ni powder, Fe powder, and activated carbon [11]. Oligomers ranging from C2 to C6 hydrocarbons had been produced in a relatively high selectivity depending on the nature of the catalyst, microwave radiation frequency, power level, and the presence of He as a diluent gas.

Nickel catalysts have been shown to be highly selective and effective catalysts to lower the activation energy of 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.

Meanwhile, Raney nickel catalysts have been used for several decades in numerous reduction and hydrogenation

---

[*] Corresponding author.
E-mail address: suib@uconnvm.uconn.edu (S.L. Suib).

0021-9517/03/$ – see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/S0021-9517(03)00083-6

reactions such as the saturation of C–C multiple bonds and aromatic rings and the reduction of aldehydes and ketones to corresponding alcohols. They are also used in various reactions in the absence of hydrogen in the gaseous phase and as an active phase of fuel cell electrodes. Raney nickel catalysts are distinguished by high activity and often by high selectivity. The nature of these phenomena is influenced by the high dispersion and strong lattice distortion of Raney nickel and by the presence of a large amount of hydrogen in an active form. Traditionally they are produced by the removal of aluminum from a Ni/Al alloy with a strong alkaline solution. The residue after leaching of the Al component consists mainly of Ni in a highly dispersed state (surface areas of 50 to 120 m^2/g).

Despite the wide use of Raney nickel, there are no publications on the activity of this catalyst in the oligomerization of methane using microwave radiation. In this work, we studied the effects of power, irradiation time, and nature of Raney nickel on the oligomerization of methane using microwave heating as energy source. Furthermore, characterization of the catalyst has been done before and after reaction in order to understand the product distribution that was observed.

2. Experimental

2.1. Microwave apparatus and gas system

The reaction was carried out in continuous flow operation in a straight $\frac{3}{8}$-in. quartz reactor, which was placed in the microwave apparatus single-mode resonant cavity as shown in Fig. 1. An ASTEX microwave power source Model GL139 with a magnetron type GL 130WC, a 3 stub tuner Model AX3041, and an ASTEX applicator Model AX7020 were used for these experiments. This power supply operates within a range of 0 to 1250 W at a frequency of 2.54 GHz, emitting pulses with a periodicity of 8.3 ms.

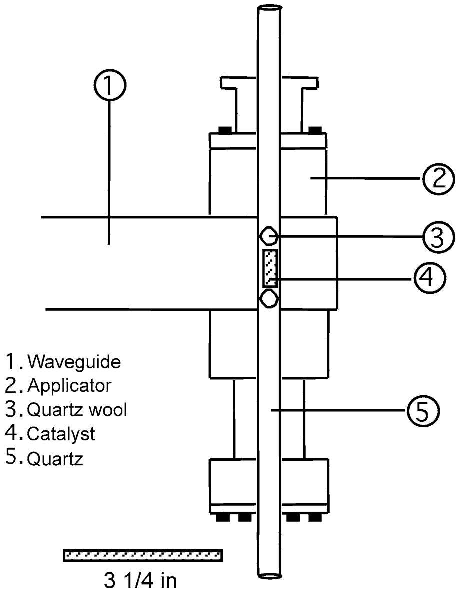


Fig. 1. Microwave applicator and reactor.

High-purity (HP) grade methane obtained from Matheson and ultrahigh purity (UHP) helium and hydrogen purchased from Airgas were used. Gases were mixed on line in a gas-mixing panel as noted in our previous work [11]. An electronic J&W Scientific Gas Flowmeter 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 was used to control the flow rates.

2.2. Catalyst

2.2.1. Preparation

The catalyst used for this study was activated Raney nickel purchased from Acros Organics. Raney nickel was supplied as 50% slurry in water, 10.5% aluminum-balance content. Particle size ranged from 5 to 128 μm. The slurry was desiccated using silica gel under 2.67×10^{-3} bar and room temperature for 6 h. Handling of the catalyst was always carried out in a nitrogen atmosphere glove bag. After drying, 100 mg Raney nickel powder was placed inside the reactor with high-purity quartz wool on either side of the catalyst bed. Helium was flushed for 30 min through the reactor to purge the air still present in the system.

2.2.2. Pretreatment

Although, the catalyst was handled under a nitrogen atmosphere, some exposure to air may have occurred when transferring the reactor from the glove bag to the microwave apparatus and while connecting fittings. For activity comparison, additional experiments were done with a reduced catalyst. Raney nickel was reduced in situ with UHP hydrogen at 300 °C for 2 h. Feed was 30% hydrogen in helium and the total flow rate was 15 mL/min.

All experiments were run with a mixture of 3 mL/min pure methane and 9 mL/min helium at atmospheric pressure. Samples for product analyses were taken at 5, 10, and 15 min of reaction time over a power range of 250 to 1125 W.

2.3. Product analysis

Products were trapped with a gas-sampling valve and analyzed by an HP5890 Series II gas chromatograph, which was equipped with a mass detector. 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), and then reenter the precolumn. Subsequently, gases are sent through a 30:1 split and finally to a Poraplot Q column (HP Poraplot Q 25 m × 0.32 mm). Afterward, individual gases pass through an interface to a HP 5971A mass selective detector where they are identified and quantified. The detector used for the MSD is a continuous dynode electron multiplier connected to a quadrupole mass filter.

The total conversion of methane was estimated by carbon balance calculations. 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 ($C_{i\mathrm{s}}$).

The compounds that can be detected using gas chromatography as noted above are methane, carbon dioxide, carbon monoxide; $C_{2\mathrm{s}}$, ethylene, acetylene, and ethane; $C_{3\mathrm{s}}$, propene, propane, 1,2-propadiene, propyne; $C_{4\mathrm{s}}$, 2-methylpropane, 2-butene, 1-buten-3-yne, 1,2-butadiene, butadiene, 1-butyne, 2-butyne; $C_{5\mathrm{s}}$, 3-pentene-1-yne; C_6, benzene; $C_{7\mathrm{s}}$, toluene, $C_{8\mathrm{s}}$, ethylbenzene, ethynylbenzene, and ethenylbenzene.

The conversion in percentage is calculated as follows,

$$X_{\mathrm{CH_4}}\ (\%) = (C_{\mathrm{T}} - C_{\mathrm{CH_4\,exit}})/C_{\mathrm{T}} \times 100,$$

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.,

$$C_{\mathrm{T}} = \sum n_i C_i.$$

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

$$S_i\ (\%) = \left(\sum n_i C_i\right) \Big/ (C_{\mathrm{T}} - C_{\mathrm{CH_4\,exit}}) \times 100.$$

2.4. Characterization

2.4.1. BET surface area analysis

Surface areas of Raney nickel samples before and after reactions were determined by Brunauer–Emmett–Teller measurements (BET). The instrument used was a NOVA 1000 Gas Sorption BET unit, purchased from Quantachrome. A five-point BET method for nitrogen adsorption was used.

2.4.2. Scanning electron microscopy

SEM photographs of Raney nickel samples before and after reactions were taken on an AMRAY 1810D scanning electronic microscope, using a tungsten filament and an acceleration potential of 16 and 17 kV.

2.4.3. X-ray photoelectron spectroscopy

The XPS data were acquired using a Leybold-Heraeus LHS-10 instrument equipped with an Al KR X-ray source and a SPECS EA 10MCD energy analyzer. Data for all detailed spectra were obtained using a Mg X-ray anode (1253.6 eV) and a constant energy analyzer pass of 59.21 eV. The ion gun was oriented 30° above the sample plane. Raney nickel samples before and after reactions were analyzed.

2.4.4. Temperature-programmed desorption and reduction

TPD and TPR experiments were used to study the nature of the adsorbed species on the catalyst surface. The reactor used for TPD studies was homemade with a thermocouple inserted as close to the catalyst as possible. Eighty milligrams of catalyst was used for each analysis. Ultrahigh purity helium was used as the carrier gas at 30 mL/min. For TPR analysis the feed was 1 mL/min of ultrahigh purity hydrogen and the carrier gas was 29 mL/min of helium. In each run, the catalyst was purged with helium gas for more than 2 h at room temperature until the baseline was flat to eliminate weakly physisorbed species and then heated linearly from 25 to 825 °C at 10 °C/min. The species evolving from the catalysts during TPD were analyzed with a mass spectrometer with a quadrupole ionizing detector (MKS Instrument Inc.).

3. Results

The effects of power and irradiation time on the oligomerization of methane via microwave heating were studied using Raney nickel as catalyst and helium as diluent. Experiments were done with two different sets of Raney nickel: (1) nonreduced Raney nickel, i.e., after drying slurry; (2) reduced Raney nickel, i.e., after drying and treating with hydrogen at 300 °C for 2 h. Conversion of methane decreases from a maximum of 24% when using nonreduced catalyst to a maximum of 14% when using reduced catalyst.

When nonreduced Raney nickel was used, it required an "activation" stage at low power (250 W) for 30 min where oxygen in the system was consumed. Fig. 2 shows conversion of methane during this stage. At these conditions, only CO was produced and no other hydrocarbon. After this period, higher hydrocarbons such as $C_{3\mathrm{s}}$, C_6, and $C_{8\mathrm{s}}$ were detected with selectivities lower than 2%. When reduced Raney nickel was used, the activation stage was also required at a higher power (600 W) for 80 min and there was no product detected during this period.

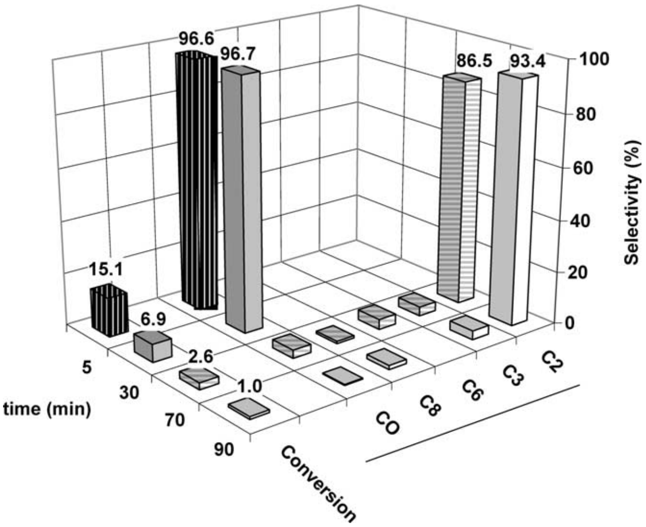


Fig. 2. Effect of irradiation time on conversion and selectivity at 250 W using nonreduced Raney nickel.

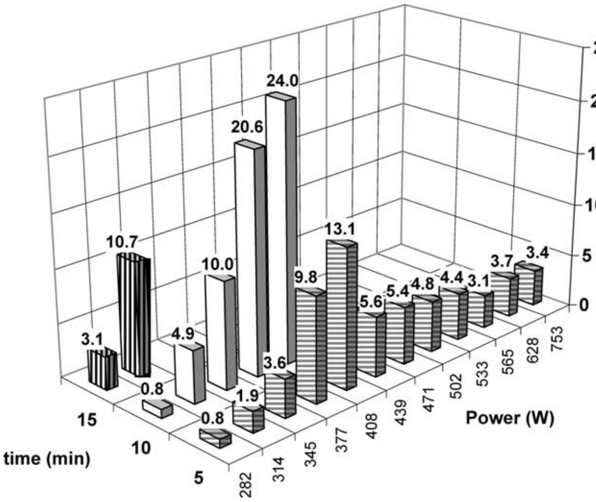


Fig. 3. Effect of applied power and irradiation time on conversion after activation stage using nonreduced Raney nickel.

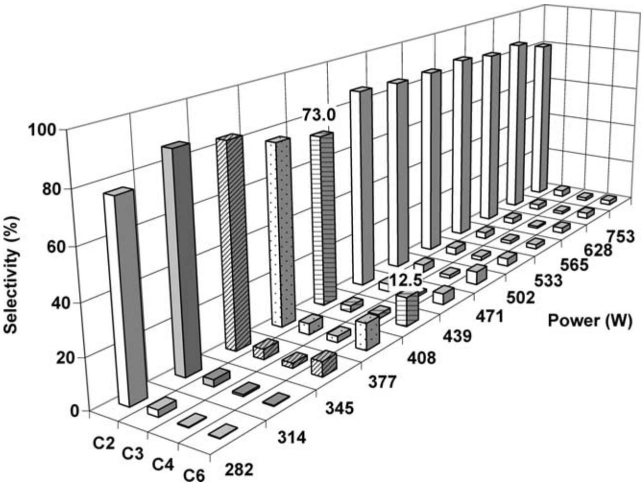


Fig. 4. Effect of applied power on selectivity at 5 min of irradiation time using nonreduced Raney nickel.

3.1. Nonreduced catalyst

When using nonreduced Raney nickel catalyst, and 25% methane diluted in helium as reactant, as power increased from 280 to 750 W at short irradiation time (5 min), conversion went through a maximum of 13% at around 400 W (Fig. 3). At this irradiation time and at all powers, the major products were C_{2s}, C_6, and C_{3s}, respectively (Fig. 4). Furthermore, at 400 W C_6 reached its maximum selectivity of 12%, while C_{2s} reached its minimum selectivity of 73%. Fig. 5 shows that when the inflection occurred, the major product among C_{2s} was ethylene with a selectivity of 37%, then acetylene (34%), and finally ethane (2%). During the maximum conversion range, i.e., 340–470 W, and 5 min irradiation time, the three most abundant products were ethylene, acetylene, and benzene, respectively. Meanwhile, for the other powers at the same irradiation time, the most significant products were ethylene and ethane.

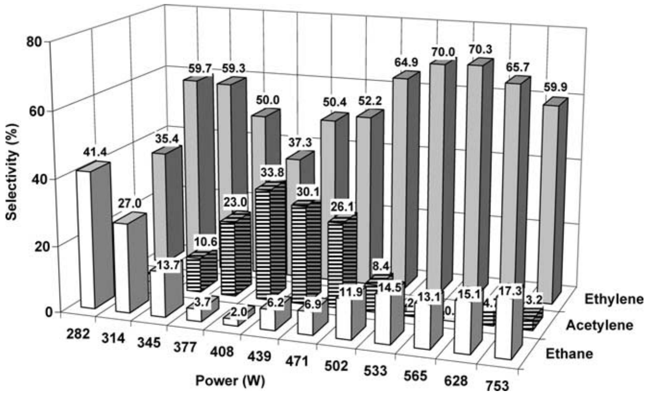


Fig. 5. Effect of applied power on C_{2S} selectivities at 5 min of irradiation time using nonreduced Raney nickel.

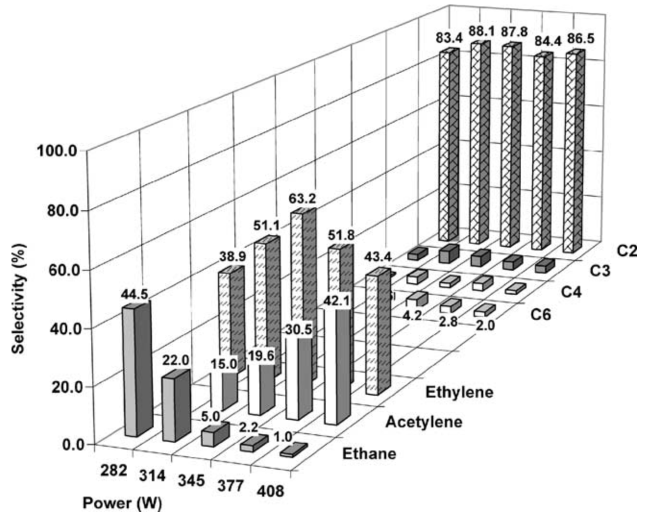


Fig. 6. Effect of applied power on selectivity at 10 min of irradiation time using nonreduced Raney nickel.

For a longer irradiation time of 10 min, the conversion increased up to 24% at about 400 W, and the major products were C_{2s} as observable in Fig. 6, with an average selectivity of 86% for all powers. The foremost products were ethylene and acetylene. The later became important as power increased as seen in Fig. 6. When power was increased above 400 W, the reactor melted after 8 min. Samples were collected only up to 300 W for 15 min of irradiation time. The most abundant products for these conditions were ethylene with a selectivity of 50%, acetylene (24%), and benzene (13%). Beyond 300 W the reactor melted after 10 min.

3.2. Reduced catalyst

Raney nickel was pretreated with hydrogen for 2 h at 300 °C. After reduction, the catalyst was purged with helium for 3 h to eliminate excess of hydrogen. For this reaction the feed was 25% of methane in helium. Conversion to products was higher than that of nonreduced catalyst at lower powers. However, the maximum power that could be applied was 280 W. After 280 W, the reactor and catalyst melted. Fig. 7

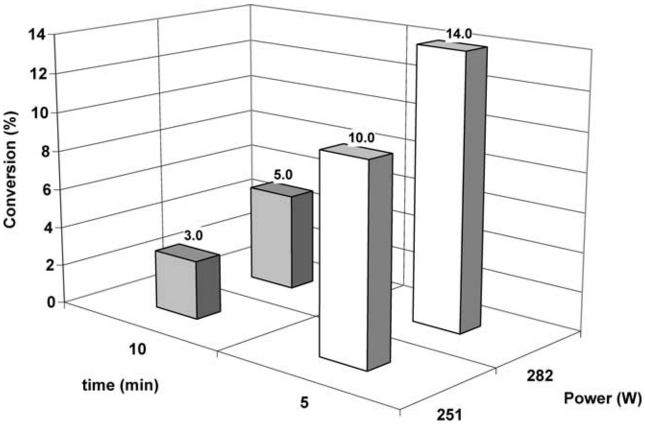


Fig. 7. Effect of applied power and irradiation time on conversion using reduced Raney nickel.

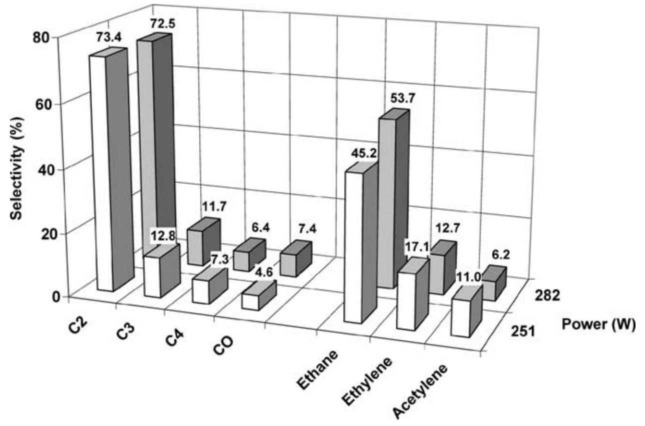


Fig. 8. Effect of applied power on selectivity at 5 min of irradiation time using reduced Raney nickel.

shows that the maximum conversion (14%) was reached at 280 W after 5 min of irradiation time. As time increased, deactivation occurred and conversion decreased from 14 to about 4%. Selectivities toward C_{2s} decreased from 80 to about 70% compared to nonreduced catalyst at short and medium irradiation times. The major change was the product distribution among C_{2s}. Fig. 8 shows that the main product for the reduced catalyst was ethane (54%) followed by ethylene (13%). C_{3s} (mostly propane) was comparatively more abundant than acetylene. Benzene was not detected.

4. Discussion

Oligomerization of methane via microwave heating was obtained using Raney nickel catalysts. In a previous publication [12] we reported that the reaction mechanism most probably involves the formation of free radicals, specially methylene and CH radicals. Some of the reactions proposed by Wan et al. [10] are

$$CH_4 \rightarrow :CH_2 + H_2, \tag{1}$$

$$:CH_2 \rightarrow :CH + :H, \tag{2}$$

$$2CH_4 \rightarrow C_2H_4 + 2H_2, \tag{3}$$

$$2CH_4 \rightarrow C_2H_2 + 3H_2, \tag{4}$$

$$C_2H_4 + H_2 \rightarrow C_2H_6, \tag{5}$$

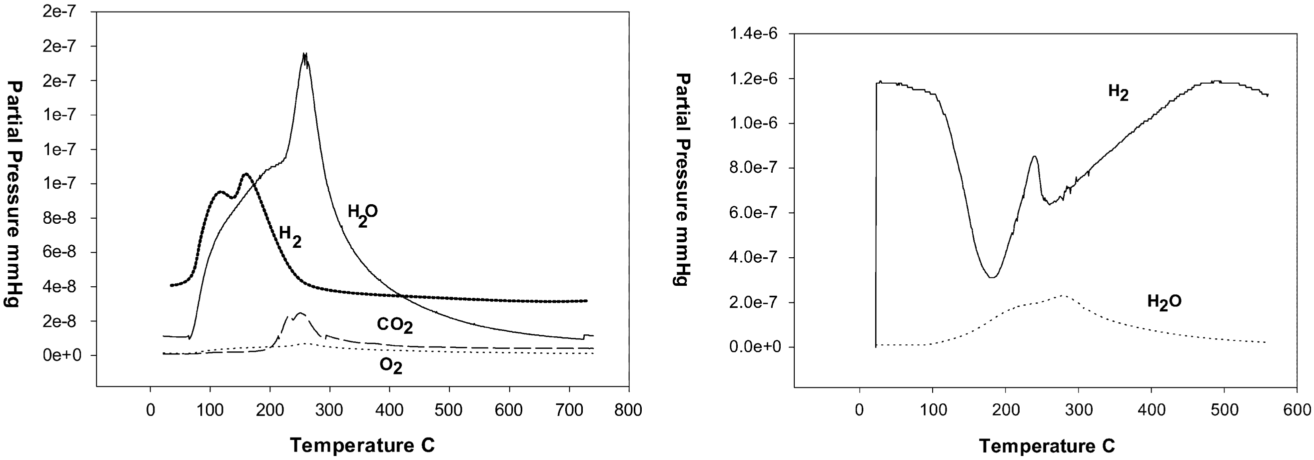
$$3C_2H_2 \rightarrow C_6H_6. \tag{6}$$

In general, the most noticeable products were ethylene, acetylene, and benzene for nonreduced Raney nickel. For reduced Raney nickel the most important products were ethane and ethylene. TPD studies indicate two forms of adsorbed hydrogen, one of which is a weakly bound molecular form, and the other is a strongly bound atomic form [13]. Reduction of Raney nickel increases the amount of chemisorbed hydrogen on the surface of the catalyst [14]. This higher concentration of reactive hydrogen on the surface favors the formation of saturated hydrocarbons such as ethane, explaining the product distribution observed in the reduced Raney nickel experiments.

Comparing the results of this study with the results of the same reaction using nickel power, it is unambiguous that the lifetime of Raney nickel is about one-third of the lifetime of nickel powder. The activity of Raney nickel is also remarkably higher than that of nickel powder. Raney nickel gives higher conversions at the same moderate power (24% vs less than 10% at about 400 W). Moreover, products are detected at a lower power (300 W) than that of the nickel powder experiments (400 W) [11].

Even though handling of Raney nickel was carried out in a glove bag with an inert atmosphere, some oxidation might have occurred on the surface of the catalyst while transferring the reactor to the microwave unit. TPD studies revealed the presence of a small amount of oxygen on the surface as well as a larger amount of CO_2 and an even larger amount of H_2O (Fig. 9a). Clearly some water remains in the Raney nickel after the drying process. These absorbed species on the surface supply the source of oxygen to form CO, which was detected in the activation stage of nonreduced catalyst. Desorption of hydrogen from the catalyst confirmed the presence of two forms of hydrogen. Weakly adsorbed hydrogen evolved at 110 °C is the reactive hydrogen (Fig. 9a), as already noted by Barbier and co-workers [15]. The second hydrogen peak is a strongly bound dissociative form, which desorbs at around 165 °C. On the other hand, the reaction temperatures for the 200–400 W range are in the order or 800–1000 °C, according to previous work published elsewhere [11]. Therefore, all hydrogen from the catalyst is quickly consumed to produce ethane as a major product. Once the highly reactive hydrogen is consumed, the major products are acetylene and benzene, respectively, at about 400 W. Thereafter the catalyst deactivates as observed in Fig. 3.

Mikhailenko et al. [14] reported that redox treatment on Raney nickel causes a redistribution of the energy inhomogeneity of the surface, shifting the desorption peaks of hydrogen to a lower temperature, and the total amount of hydrogen desorbed decreases. As discussed later, the BET



(a) (b)

Fig. 9. (a) Temperature-programmed desorption analysis of fresh Raney nickel. (b) Temperature-programmed reduction analysis of fresh Raney nickel.

surface area decreases, leading to a decrease in the amount of hydrogen adsorbed, mainly at the expense of strongly bound form. This more readily available reactive hydrogen explains the formation of ethane at lower power for the case of reduced Raney nickel. While hydrogen is being consumed Raney nickel is losing its activity most probably due to sintering. Once hydrogen is finished the catalyst also has sintered, significantly plummeting conversion.

In general, nickel catalysts strongly absorb microwave energy, providing the necessary kinetic energy for the surface electrons to enhance surface chemical reactions. The energy absorbed by the surface metallic sites is transformed from a rapid oscillating electrical field into thermal energy [12]. Taking into account that pretreatment on Raney nickel causes redistribution of the energy inhomogeneity on the surface [14], different heating patterns for the two catalysts at the same microwave power are expected. Therefore, systematic effects of the microwave absorption on heating rates can also be responsible for changes in product distribution and activities of the catalysts.

An attempt to quantify the temperature during the reaction was performed in previous studies [11]. For those experiments using nickel powder, temperature was not measured in situ since the thermocouple will interfere with the microwave field forming arcs during the reaction. Despite limitations of our system to accurately measure reaction temperatures under microwave radiation, approximate measurements using the following procedure were carried out: after steady state was achieved under reaction conditions, the microwave power was shut off, followed by the insertion of the thermocouple in the catalyst bed to obtain information about temperatures at different applied powers. The method is not completely accurate but gives an idea of the temperature levels in the system as seen in Fig. 10.

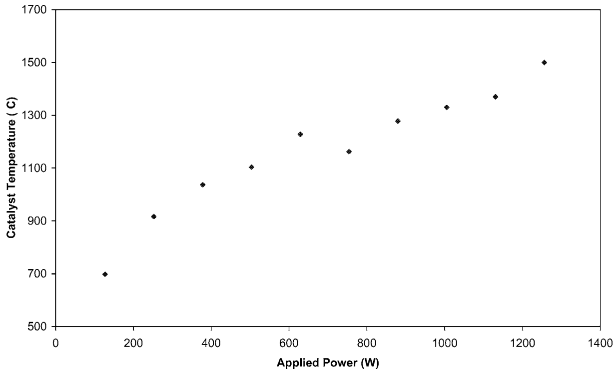
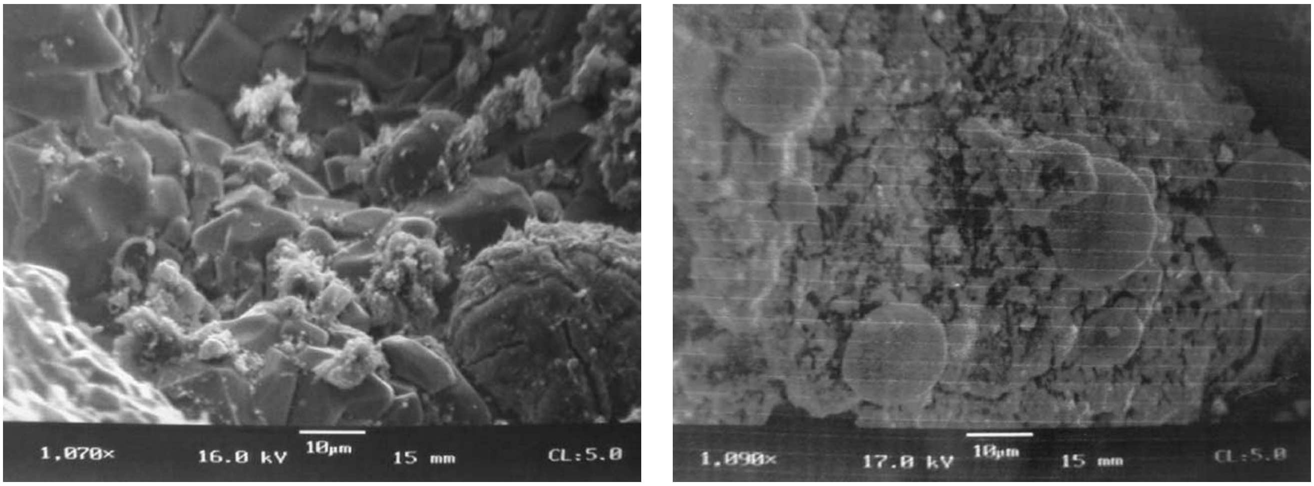


Fig. 10. Effect of applied power on catalyst temperature using nickel powder.

BET studies on the catalyst, performed before and after reaction, showed a considerable loss of surface area. Fresh dried Raney nickel had a surface area of 60.42 m^2/g. After reaction the surface area of the catalyst decreased by 65% of the initial value, i.e., 21.15 m^2/g. This surface area loss suggested deactivation of the catalyst by sintering, which is confirmed by scanning electron microscopy. SEM photographs in Fig. 11 revealed the following: (a) Fresh Raney nickel consisted of large particles (about 10 µm and above) with a platelike morphology. Some of them have agglomerated to form larger units (size up to 200 µm). (b) After the reaction Raney nickel sintered giving a bulk-like appearance. Samples for after reaction photographs were taken at intermediate power (around 400 W) and 5 min of irradiation time. Beyond this point, the catalyst was mostly melted. Mikhailenko et al. [14] found out that partial sintering of Raney nickel occurred during the reduction process explaining the decrease in activity with respect to nonreduced catalyst.

General observations from XPS studies can be seen in Table 1. The amount of zero-valent metal on Raney nickel surface was not enough to resolve the contribution to the spectra and differentiate the metal phase from the contribution of nickel oxide. Despite the small amount of nickel metal, the catalyst was still very active compared to bulk nickel [11]. In addition to the high surface area of Raney nickel there are other species on the surface of the catalyst



(a) (b)

Fig. 11. (a) Scanning electron microscopy photograph of Raney nickel before reaction. (b) Scanning electron microscopy photograph of Raney nickel after reaction.

Table 1
X-ray photoelectron spectroscopy analysis for Raney nickel

	Ni	C	O	Al^{3+}	Al^0
Fresh	29.64*	7.85**	57.97	2.27	2.27
After reaction	0.14	88.15***	11.71		

Atom ratios: $^*Ni^{2+}$ and Ni^0; **C–O and C–O_2; ***Aliph + Olef.

that might be responsible for high activity. Residual metallic aluminum and its corresponding oxides are also present on the surface and can play an important role in the activity of the catalyst as suggested by Birkenstock et al. [16]. In addition, Diskin et al. [17] observed that nickel oxides on the surface of the catalyst can be active sites for the activation of methane as well as nickel metal. XPS also detected different forms of oxygen on the surface of the fresh catalyst. Sources of oxygen might be assigned to H_2O, $Ni(OH)_2$, NiO, and Al_2O_3 which would be in agreement with Yoshino et al. [18] and with the data obtained from TPR analysis (Fig. 9b). Reduction of NiO generally proceeds within the 280–300 °C range [19]. The first hydrogen peak of the TPR plot most probably corresponds to consumption of hydrogen to reduce $Ni(OH)_2$, which is present in large amounts and requires lower reduction activation energy than that of the more stable NiO [19]. After reaction catalyst analysis showed a very small amount of nickel on the surface and almost 90% of carbonaceous species. This finding confirms that deactivation of the catalyst also is due to blocking of active sites with carbon. Deactivation mechanisms responsible for loss of Raney nickel catalysts in methanation reactions are sintering and fouling (series and parallel) [20]. Series fouling occurs when the produced CO generates a side reaction to form carbon. The process can be illustrated by

$$2CO + s \leftrightarrow s \cdot C + CO_2, \tag{7}$$

where s is the catalytic active site.

CO is produced mainly during the initial stage of the oligomerization of methane as seen in Fig. 2. Besides, it has been seen that low temperatures at low power favor the decomposition of carbon monoxide [20]. When power increases during the reaction, high temperatures favor the decomposition of methane deactivating the catalyst by a parallel fouling mechanism. Eq. (8) describes this process,

$$CH_4 + s \leftrightarrow s \cdot C + 2H_2, \tag{8}$$

where s is the catalytic active site.

Finally, at the end of the reaction the temperature is high enough to favor sintering of the catalyst as seen in Fig. 11, rapidly ceasing the catalytic activity of Raney nickel.

5. Conclusion

Raney nickel has been shown to be a selective catalyst in the oligomerization of methane via microwave heating. The maximum conversion achieved in this reaction was 24% at 400 W and 10 min of microwave irradiation time. In our previous work [11] with regular nickel powder comparable conversion and selectivities were obtained only at high power (above 700 W) and long microwave irradiation time (above 20 min). Ethylene, benzene, and ethane have been prepared selectively under different conditions. Selectivities as high as 71, 13, and 54% have been obtained for ethylene, benzene, and ethane, respectively. Short microwave irradiation times and high power (above 530 W) enhance the formation of ethylene, whereas intermediate power (400 W) favors the formation of benzene. Pretreatment of the catalyst with hydrogen reduction increases the formation of ethane at low and intermediate power. Several mechanisms are responsible for deactivation of the catalyst. Parallel fouling most probably is present at the beginning of the reaction when CO is formed. Later in the reaction, while temperature increases, decomposition of methane might cause deactivation by series fouling. Finally, sintering of Raney nickel occurs at higher temperatures terminating the reaction.

Acknowledgments

The authors thank the National Science Foundation and the Electrical Power Research Institute under Grant CTS-9413394 of the joint NSF/EPRI Initiative on Microwave Induced Reactions.

References

[1] M.S. Ioffe, S.D. Pollington, J.K.S. Wan, J. Catal. 151 (1995) 349–354.

[2] S.D. Pollington, M.S. Ioffe, M. Westergaard, J.K.S. Wan, Res. Chem. Intermediates 21 (1995) 59–62.

[3] C. Chen, D. Hong, S. Dai, J. Kan, J. Chem. Soc., Faraday Trans. 91 (1995) 1179–1184.

[4] J.R. Anderson, Appl. Catal. 47 (1989) 177.

[5] H. Mimoun, New J. Chem. 11 (1987) 513.

[6] J.K. Hoyano, A.D. McMaster, W.A.G. Graham, J. Am. Chem. Soc. 105 (1993) 7190.

[7] L.C. Kao, A.C. Hutson, A. Sen, J. Am. Chem. Soc. 113 (1991) 700.

[8] J.S. Lee, S.T. Oyama, Catal. Rev. Sci. Eng. 30 (1988) 249.

[9] Y. Amenomiya, V.I. Birss, J. Goledzinowski, J. Galuszka, A.R. Sanger, Catal. Rev. Sci. Eng. 32 (1990) 163.

[10] J.K.S. Wan, M.Y. Tse, H. Husby, M.C. Depew, J. Microwave Power Electromagn. Energy 25 (1990) 32–38.

[11] C. Marun, L.D. Conde, S.L. Suib, J. Phys. Chem. A 103 (1999) 4332–4340.

[12] L.D. Conde, C. Marun, S.L. Suib, Z. Fathi, J. Catal. 204 (2001) 324–332.

[13] F. Hochard, H. Jobic, J. Massardier, A.J. Renouprez, J. Mol. Catal. A: Chem. 95 (1995) 165–172.

[14] S.D. Mikhailenko, T.A. Khodareva, E.V. Leongardt, A.I. Lyashenko, J. Catal. 141 (1993) 688–699.

[15] P. Marecot, E. Paraiso, J.M. Dumas, J. Barbier, Appl. Catal. 74 (1991) 261–272.

[16] U. Birkenstock, R. Holm, B. Reinfandt, S. Storp, J. Catal. 93 (1985) 55–67.

[17] A.M. Diskin, R.H. Cunningham, R.M. Ormerod, Catal. Today 46 (1998) 147–154.

[18] T. Yoshino, T. Abe, S. Abe, I. Nakabayashi, J. Catal. 118 (1989) 436–442.

[19] D.A.M. Monti, A. Baiker, J. Catal. 83 (1983) 323–335.

[20] R.R. Schehl, H.W. Pennline, A.J. Youngbloed, M.J. Baird, J.P. Strakey, W.P. Haynes, Deactivation of Raney Nickel Methanation Catalyst, Energy Research and Development Administration, Pittsburgh Energy Research Center, 1977.