JOURNAL OF CATALYSIS **179,** 326–334 (1998)
ARTICLE NO. CA982225

Nonoxidative Methane Conversion to Acetylene over Zeolite in a Low Temperature Plasma

Chang-jun Liu, Richard Mallinson, and Lance Lobban[1]

Institute for Gas Utilization Technologies and School of Chemical Engineering and Materials Science, The University of Oklahoma, Norman, Oklahoma 73019

Received December 8, 1997; revised July 9, 1998; accepted July 10, 1998

Previous investigations have found that the plasma catalytic conversion of methane is a low-temperature process for the activation of methane, the major component of natural gas. In this paper, the production of acetylene via plasma catalytic conversion of methane over NaY zeolite is discussed. Hydrogen is produced as a by-product during this plasma catalytic methane conversion. A methane/hydrogen feed with oxygen as an additive and helium as a diluent has been studied in this investigation. The $CH_4/H_2/O_2$ system is found to be more selective for the production of C_2 hydrocarbons, compared to the CH_4/O_2, CH_4/H_2O, and CH_4/CO_2 systems reported previously. A higher hydrogen concentration feed is more favorable for acetylene formation. The selectivity and yield of C_2 hydrocarbons are related to the hydrogen feed rate, gas temperature, concentration of oxygen additive, and flowrate. The highest yield of C_2 hydrocarbons (32%) is obtained at the lowest flowrate used (10 cm^3/s; residence time ~2.3 s). A reaction mechanism is also presented to explain the experimental results. © 1998 Academic Press

1. INTRODUCTION

With large increases in natural gas reserves proven worldwide, it can be expected that natural gas will play an increasingly important role in energy and chemicals supplies in the 21st century. The production of hydrogen from natural gas has also received more attention. Catalytic steam or CO_2 reforming of methane, the principal component of natural gas, is the principal process for hydrogen production. About 50% of all hydrogen is produced from natural gas, and 40% of this is produced by steam reforming (1). Hydrogen is an important feedstock for the synthesis of ammonia, methanol, hydrochloric acid, and so on. Hydrogen should become the ultimate nonpolluting fuel, although it appears that initially, at least, it will be produced primarily from natural gas. There are two reversible reactions involved in methane steam reforming:

$$CH_4 + H_2O \rightleftarrows CO + 3\,H_2, \quad \Delta H_{298} = 206 \text{ kJ mol}^{-1}, \quad [1]$$

$$CO + H_2O \rightleftarrows CO_2 + H_2, \quad \Delta H_{298} = -41 \text{ kJ mol}^{-1}. \quad [2]$$

The overall reaction is:

$$CH_4 + 2H_2O \rightleftarrows CO_2 + 4\,H_2, \quad \Delta H_{298} = 165 \text{ kJ mol}^{-1}. \quad [3]$$

Methane steam reforming is thermodynamically favorable at high temperatures (the operating temperature is usually higher than 1073 K) and low pressures. An intensive energy input is required due to the high temperature operation, while the by-product, CO_2, is a major greenhouse gas with little value.

CO_2 reforming of methane has similar thermodynamic and equilibrium characteristics to the steam reforming process but it produces a synthesis gas with a lower H_2/CO ratio:

$$CH_4 + CO_2 \rightleftarrows 2\,CO + 2\,H_2, \quad \Delta H_{298} = 247 \text{ kJ mol}^{-1}. \quad [4]$$

In addition to the intensive energy input, carbon formation is another problem with CO_2 reforming (2). Extensive investigations on the direct conversion of methane via pyrolysis, including microwave irradiation and plasma techniques, with hydrogen as one of products, are being conducted (3–7). Methane can be converted directly to C_2 hydrocarbons and hydrogen via pyrolysis or thermal coupling:

$$2CH_4 \rightarrow C_2H_2 + 3\,H_2, \quad \Delta H_{298} = 376.5 \text{ kJ mol}^{-1}, \quad [5]$$

$$2CH_4 \rightarrow C_2H_4 + 2\,H_2, \quad \Delta H_{298} = 202.3 \text{ kJ mol}^{-1}, \quad [6]$$

$$2CH_4 \rightarrow C_2H_6 + H_2, \quad \Delta H_{298} = 65.1 \text{ kJ mol}^{-1}. \quad [7]$$

All these reactions are highly endothermic, and high temperature operation is required to obtain favorable thermodynamics. A very high yield of acetylene (>85%) and more

---

[1] To whom the correspondence should be addressed. E-mail: llobban@ou.edu.

0021-9517/98 $25.00

than 90% selectivity of C_2 hydrocarbons can be achieved from methane at temperatures higher than 2000 K and reaction times less than 0.01 s (3). A longer reaction time may lead to excessive carbon formation. Thermal cracking of methane in the presence of hydrogen has also been conducted (4) in a tubular flow reactor under atmospheric pressure with the temperature between 1450 and 1500 K. The products of thermal cracking include C_2 hydrocarbons (C_2H_2, C_2H_4, and C_2H_6) and coke with a small amount of $C_3 \sim C_5$ and C_{10}^+ hydrocarbons. Dilution with hydrogen increases selectivities and yields of C_2 hydrocarbons and reduces the formation of coke at the expense of methane conversion. The disadvantage of methane pyrolysis is that the high reaction temperature requires an intensive energy input and a high operating cost (including reactor materials, heat transfer, and heat recovery). These severe conditions also favor very large plants for maximum efficiency. To reduce energy costs, one may use electric power in a plasma process instead of thermal processing (5). A sufficiently high methane conversion (as high as 85%) at lower gas temperatures has been achieved using microwave plasmas (6,7). The energy efficiency reported was 2–8% (the energy efficiency is defined as the ratio of the minimum free energy required to convert methane to C_2 hydrocarbons and hydrogen to the actual microwave energy input into the system) (6). Methane pyrolysis under pulsed microwave radiation in the presence of solid catalysts has also shown selective conversion of methane to acetylene at a lower gas temperature (1370–1470 K) (8,9), compared to the thermal coupling of methane. The commercial arc discharge process for the acetylene production from natural gas has been carried out for many years by Du Pont and by the Huels process (3). A thermodynamic and kinetic analysis of plasma chemistry shows that a high temperature (>3000 K) would be favorable for the yield of acetylene (10,11). However, this high temperature also requires high operating costs and energy consumption (3). In practice, microwave irradiation or arc discharges may not be energy-efficient because of the energy that goes into gas heating (e.g., they still result in essentially a thermal process). To drive reactions [5]–[7] at much lower gas temperatures, a cold or "nonequilibrium" plasma can be applied (12). The cold plasma is characterized by high electron temperatures and low bulk gas temperatures (as low as room temperature). Therefore, gas heating is not a significant energy sink with cold plasmas. We have previously reported the methane conversion to higher hydrocarbons via corona discharge (13,14) and plasma catalytic conversion (15–17). We have found that the corona discharge is an efficient and effective technique for the low gas temperature (as low as 233 K) methane conversion. In this paper, we discuss the production of acetylene and hydrogen from methane and hydrogen via nonequilibrium plasma (corona discharge) catalytic methane conversion over NaY zeolite.

2. EXPERIMENTAL METHODS

The experimental apparatus is the same as previously described (14–17). The reactor was a quartz tube with an ID of 7 mm. The reactor was heated (when needed) by a cylindrical furnace placed around the reactor. An Omega K-type thermocouple was attached to the outside wall of the reactor of monitor and control the gas reaction temperature. The temperature measured in this way has been calibrated against the internal temperature and has been discussed elsewhere (13,14). When a low gas temperature was employed for the gas discharge reactions, the reactor was cooled outside by flowing room-temperature air. For the low temperature reactions (less than 373 K), the gas discharge is usually initiated at room temperature and the gas is self-heated by the plasma. The gas temperature can be controlled by adjusting the flow rate of the flowing room air. All the experiments were operated at atmospheric pressure. The flowrates of feed gases methane, hydrogen, oxygen, and helium were regulated by mass flow controllers (Porter Instrument Co. model 201). The feed gas was analyzed by an on-line gas chromatograph (HP 5890) with a thermal conductivity detector. The exhaust gas from the reactor flowed through a condenser to remove condensable liquid and was then analyzed by the gas chromatograph. A CARLE series 400 gas chromatograph (EG&G Chandler) was used for the detection of hydrogen. For this system, the methane and oxygen conversions are defined as:

$$CH_4 \text{ conversion} = (\text{moles of } CH_4 \text{ consumed/moles of } CH_4 \text{ introduced}) \times 100\%;$$

$$O_2 \text{ conversion} = (\text{moles of } O_2 \text{ consumed/moles of } O_2 \text{ introduced}) \times 100\%.$$

The selectivities and yields of C_2 hydrocarbons are:

$$\text{Selectivity of } C_2H_6 = 2 \times (\text{moles of } C_2H_6 \text{ formed/moles of } CH_4 \text{ consumed}) \times 100\%;$$

$$\text{Selectivity of } C_2H_4 = 2 \times (\text{moles of } C_2H_4 \text{ formed/moles of } CH_4 \text{ consumed}) \times 100\%;$$

$$\text{Selectivity of } C_2H_2 = 2 \times (\text{moles of } C_2H_2 \text{ formed/moles of } CH_4 \text{ consumed}) \times 100\%;$$

$$\text{Yield of } C_2 \text{ hydrocarbons} = CH_4 \text{ conversion} \times \sum (\text{selectivities of } C_2H_2, C_2H_4, C_2H_6).$$

The selectivity and yield of hydrogen are:

$$\text{Selectivity of } H_2 = 0.5 \times (\text{moles of } H_2 \text{ formed/moles of } CH_4 \text{ consumed}) \times 100\%;$$

$$\text{Yield of } H_2 = CH_4 \text{ conversion} \times \text{Selectivity of } H_2.$$

A DC corona discharge, which is a cold plasma, was used for this research on plasma catalytic methane conversion. In the present reactor design, the stable high electric field characteristics of a wire electrode and stable hydrodynamics of the DC corona discharge are used to achieve the plasma catalytic conversion of methane. The ionized gases are generated in gap between two stainless steel electrodes. The upper wire electrode is centered axially within the reactor tube, while the lower electrode is a circular plate with holes for gas to flow through and positioned perpendicular to the reactor axis and 10 mm below the tip of the wire electrode. The catalyst bed is about 8 mm deep; thus the wire electrode is situated about 2 mm above the catalyst bed and a remote corona is present (15). The DC corona discharge is created using a high voltage power supply (Model 210-50R, Bertan Associates Inc.). The lower plate electrode is always held at a potential of zero volts (i.e., grounded). The catalyst used here is NaY zeolite in a powder form (<80 mesh). NaY zeolite was used because it was found to give the highest yields of C_2 hydrocarbons in our previous studies. The preparation and characterization of this NaY zeolite have been discussed elsewhere (15–17).

3. RESULTS AND DISCUSSIONS

3.1. *Role of the Catalyst*

Our previous investigations have established that the catalyst plays an important role in the plasma-modified reactions. The catalyst stabilizes the corona discharge at lower temperatures and voltages than would be possible in the absence of the catalyst. Reaction in the presence of catalyst and discharge yields results significantly different than those obtainable with either the discharge or the catalyst alone. Microdischarges between catalyst particles may be partially responsible for the observed conversion and selectivity. A comparison of the results from two experiments, the first with 0.1 g of catalyst, the second with 0.05 g of catalyst, shows that all of the catalyst in the bed is not uniformly utilized. In both experiments, the spacing between the electrodes was identical, as were the feed composition and flow rate. The feed flow rates of the various gases were: CH_4, 1.5 sccm; H_2, 1.5 sccm; O_2, 0.15 sccm; and He, 12 sccm. The corona discharge was established using an applied voltage of 7 kV and an applied power of 8.4 W. The results are summarized in Table 1. It is believed that the catalyst surface in contact with the plasma is important for the homogeneous plasma characteristics (and therefore the homogeneous activation of the methane). Therefore, the methane conversion rates are similar for the two experiments. The higher C_2 selectivities when 0.1 g of catalyst is used may be due to greater interaction between plasma species and catalyst surface, or due to greater catalyst surface area with activity modified by the discharge. When no catalyst is used under these conditions (i.e., same electrode spacing, applied voltage, and feed flow rate), the discharge is qualitatively different, with no visible streamers. As shown in Table 1, the methane conversion is much lower and no acetylene is produced. Further studies of these effects are underway.

TABLE 1

Effects of the Catalyst Amount on Methane Conversion and Selectivity

Amount of Catalyst (g)	Methane conversion rate (mmol/s - g cat)	Methane conversion (%)	Selectivities (%)			
			C_2H_6	C_2H_4	C_2H_2	H_2
0	—	12.0	26.0	—	—	29.0
0.05	0.0076	37.4	6.9	1.0	25.2	64.2
0.10	0.0039	38.0	7.1	1.7	32.3	76.2

The conversion and selectivity strongly depend on the identity of the catalyst. The presence of surface OH groups was shown to be important for good selectivity and conversion of methane in the presence of the corona discharge (15). It is believed that the corona discharge and charged plasma species may lead to charge accumulation on the catalyst surface, which could alter the electrostatic potential and/or work function of the catalyst. Reactive species chemisorption, desorption, and surface reactions could therefore be modified. To investigate the surface–methane interactions, a two-step plasma catalytic methane conversion was conducted. In the first step, methane chemisorption without plasma was performed at 523 K with 5% CH_4/helium with a total flow of 100 ml/min over NaY zeolite. In the second step, the co-reactant gas, hydrogen, oxygen, or carbon dioxide, but no methane, was passed through the catalyst bed, together with helium at a total flow of 20 ml/min. The corona discharge was generated to initiate plasma catalytic reactions. The products evolved from the plasma catalytic reactions were detected using an HP5890 GC with TCD detector. The amount of chemisorbed methane on the surface was determined by conducting step one and then oxidizing the carbon fragments at 523 K for 10 min [19] in a separate experiment. To conduct this, flowing helium (200 ml/min) was applied first to purge any nonchemisorbed methane. During the subsequent oxidation step, the carbon dioxide formed was adsorbed in a molecular sieve column. The amount of carbon dioxide collected on the molecular sieve was determined by running a TPD experiment (7.5 K/min, 20 cm^3/min He), measuring the CO_2 desorbed versus time.

The amount of methane chemisorbed on the NaY zeolite during the first step was measured using the procedure described above and is 33.23 μmol/g. In the second step, a corona discharge was generated over the NaY zeolite with chemisorbed methane to start the plasma-promoted reactions. The methane conversion reached 100%. Table 2 summarizes the reaction conditions and selectivities of products of the two-step PCMC with different co-reactants. The selectivities of products in Table 2 were evaluated directly from the GC peak areas. The hydrogen-containing plasma

TABLE 2

Measured Selectivities for Two-Step PCMC over NaY

Feed for the 2nd step	Feed ratio	Feed rate (ml/min)	Gas temp. for 2nd plasma reaction step (K)	Selectivities (%)			
				C_2H_6	C_2H_4	CH_4	CO
CO_2/He	1/39.2	20	523	5.1	2.2	84.0	8.7
O_2/He	1/49.0	20	423	3.1	0.0	79.3	17.6
He	-	20	423	0.0	0.0	100.0	0.0
H_2	-	20	423	10.0	4.1	85.9	0.0

induces the most selective production of C_2 hydrocarbons. CO_2 and O_2 containing plasmas also produce some C_2 products. Only methane was detected (without any detectable C_2 hydrocarbons) using a pure helium plasma. These results suggests that active plasma species, e.g., O^-, H, and $O(^1D)$, play an important role in the formation of higher hydrocarbons during the plasma heterogeneous methane conversion.

3.2. *Effects of Hydrogen and Reaction Mechanism*

The previous investigations on oxidative conversion of methane by gas discharges in the absence (13,18) and/or presence (14–17) of heterogeneous catalysts have shown that cold plasma methane conversion proceeds via steps involving free radicals, in which the formation of methyl radicals is the rate-controlling step. The oxygen used under those conditions will induce significant oxidation of methane and hydrocarbon products to produce carbon oxides (mostly carbon monoxide). The selectivity of higher hydrocarbons is thereby reduced. Methyl radicals also may be generated from reaction of methane with hydrogen radicals (18):

$$CH_4 + H \rightarrow CH_3 + H_2. \qquad [8]$$

Hydrogen radicals are produced relatively easily within cold plasmas (19). One may supply hydrogen instead of oxygen for initiating higher hydrocarbon formation. It can be expected that, in the absence of oxygen, 100% selectivity to higher hydrocarbons will be achieved from the methane and hydrogen plasma reactions except for possible carbon formation. In general, methyl radical formation is thought to be responsible for the initiation of radical reactions leading to higher hydrocarbon production. The methyl radical also can be formed from interaction of methane with other radicals (e.g., CH_3, O, and OH). In addition to the formation from radical reactions (e.g., reaction [8]), methyl radicals can be produced by electron–methane collisions (18). It has been shown that electronically excited CH_4 [S_1 (9.6 and 10.4 eV) and S_2 (11.7 eV)] can be the precursor of radicals CH_3, CH_2, and CH (18):

$$e\ (\varepsilon > 10\ \text{eV}) + CH_4 \rightarrow CH_4\ (S_1, S_2) + e \qquad [9]$$

$$\rightarrow CH_3 + H \qquad [10]$$

$$CH_2 + H + H \qquad [11]$$

$$\rightarrow CH_2 + H_2 \qquad [12]$$

$$CH + H_2 + H \qquad [13]$$

$$\rightarrow C + H_2 + H_2. \qquad [14]$$

The principal products formed by subsequent reactions are:

Ethane formation:

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad [15]$$

$$CH_4 + CH_2 \rightarrow C_2H_6 \qquad [16]$$

$$C_2H_6 + H \rightarrow C_2H_5 + H_2 \qquad [17]$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4; \qquad [18]$$

Ethylene formation:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad [19]$$

$$C_2H_6 \rightarrow CH_3 + CH_3 \qquad [20]$$

$$CH_3 + CH_3 \rightarrow C_2H_4 + H_2 \qquad [21]$$

$$CH_3 + CH_2 \rightarrow C_2H_4 + H \qquad [22]$$

$$CH_2 + CH_2 \rightarrow C_2H_4 \qquad [23]$$

$$CH_3 + CH_3 \rightarrow C_2H_5 + H \qquad [24]$$

$$C_2H_6 + H \rightarrow C_2H_5 + H_2 \qquad [25]$$

$$C_2H_6 + CH_3 \rightarrow CH_4 + C_2H_5 \qquad [26]$$

$$C_2H_5 + H \rightarrow CH_3 + CH_3 \qquad [27]$$

$$C_2H_5 + H \rightarrow C_2H_4 + H_2; \qquad [28]$$

Acetylene formation:

$$C_2H_4 \rightarrow C_2H_2 + H_2 \qquad [29]$$

$$CH_2 + CH_2 \rightarrow C_2H_2 + H_2 \qquad [30]$$

$$C_2H_4 + H \rightarrow C_2H_3 + H_2 \qquad [31]$$

$$C_2H_3 + H \rightarrow C_2H_2 + H_2 \qquad [32]$$

$$CH + CH \rightarrow C_2H_2 \qquad [33]$$

$$CH_2 + CH \rightarrow C_2H_2 + H. \qquad [34]$$

There are some small amounts of higher hydrocarbons (butane, pentane, etc.) detected during plasma catalytic methane conversion. These higher hydrocarbons can be produced heterogeneously via (M means catalyst surface or reactor wall):

$$C_2H_5 + CH_3 \xrightarrow{M} C_3H_8 \quad [35]$$

$$C_2H_5 + C_2H_5 \xrightarrow{M} C_4H_{10} \quad [36]$$

$$C_3H_7 + C_2H_5 \xrightarrow{M} C_5H_{12} \quad [37]$$

$$C_4H_9 + CH_3 \xrightarrow{M} C_5H_{12}. \quad [38]$$

Some ionic species, e.g., CH_4^+ and O^+, are also present during plasma catalytic reactions. Compared to radical species, the concentrations of ionic species are very small and therefore the reactions of ionic species may be ignored (18,19).

In addition, the hydrogen radical is assumed to be an essential ingredient for the removal of undesired carbon deposition which can have a negative effect on gas discharges:

$$C(s) + H \rightarrow CH \quad [39]$$

$$CH(s) + H \rightarrow CH_2. \quad [40]$$

However, it has also been found that hydrogen inhibits methane conversion by glow discharge in the absence of a catalyst (20). The reason for this inhibition by hydrogen can be explained by the reaction (3):

$$CH_3 + H_2 \rightarrow CH_4 + H. \quad [41]$$

The inhibition was also observed during the plasma catalytic methane conversion over NaY zeolite. The methane conversion and C_2 yield do not increase significantly with increasing hydrogen in the feed. A tendency to produce higher hydrocarbons during plasma catalytic reactions using hydrogen as a coreactant over NaY zeolite was also observed. A good yield of C_2 hydrocarbons can be observed only for a short time (the feed ratio of CH_4/H_2 is 1/4 with a flowrate of 50 cm^3/min). Initially, a golden spark is present in the pink glow of the streamer discharge, and good plasma catalytic activity occurs only with streamer discharges (15). The pink glow, associated with trapped electrons, was discussed previously (15,16) and was also observed during irradiation of zeolite (21). Then the streamer discharge turns to an arc-like discharge. After reaction, the catalyst particles have aggregated into larger "lumps." It is thought that polymerization occurs during discharge reactions to bind the particles together. Probably acetylene, the major hydrocarbon product, is partially polymerized under the plasma conditions (22). To stabilize and sustain the streamer discharges, a small stream of oxygen was added to the feed, a technique that has also been applied to the pyrolysis of natural gas (3). Oxygen will alter the plasma chemistry and efficiently inhibit the polymerization, probably via OH radicals (23), which can be formed by:

$$H + O_2 \rightarrow OH + O \quad [42]$$

$$OH + H_2 \rightarrow H_2O \quad [43]$$

$$H_2O + O \rightarrow OH + OH. \quad [44]$$

The disadvantage of the addition of oxygen into the plasma catalytic reactions is the formation of carbon oxides:

$$CH_3 + O \rightarrow HCHO + H \quad [45]$$

$$HCHO + O \rightarrow OH + CHO \quad [46]$$

$$CHO + O \rightarrow OH + CO \quad [47]$$

$$CHO + O \rightarrow CO_2 + H \quad [48]$$

$$HCHO + H \rightarrow H_2 + CHO \quad [49]$$

$$CHO + H \rightarrow H_2 + CO \quad [50]$$

$$HCHO + OH \rightarrow CHO + H_2O \quad [51]$$

$$CHO + OH \rightarrow CO + H_2O. \quad [52]$$

A schematic summary of the reaction pathways is shown in Fig. 1.

Figure 2 shows the effects of hydrogen in the feed on selectivities (Fig. 2a) and methane conversion and yields of desired products (Fig. 2b). The C_2 yield is about 20%, which is higher than that achieved with plasma oxidative conversion of methane (i.e., in the absence of catalyst) (15,16). It is also shown that the C_2 yield and methane conversion do not change significantly with increasing hydrogen feed concentration. Figure 2b indicates that most of C_2 products

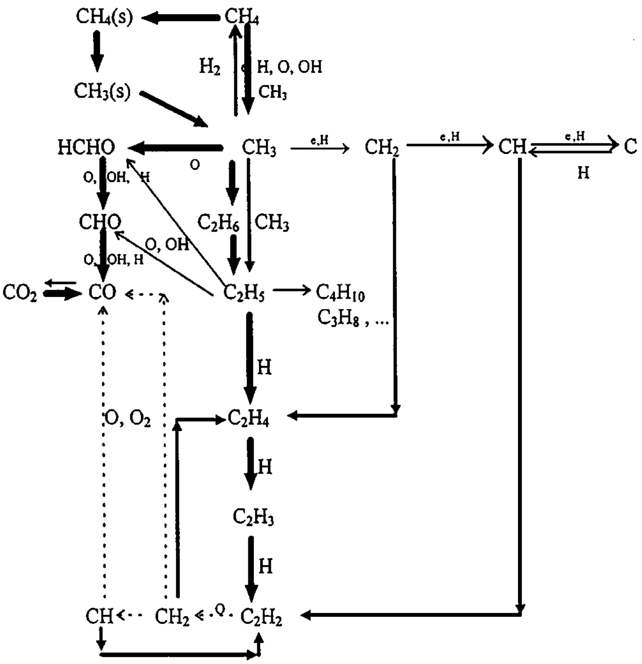

FIG. 1. Schematic representation of the overall reaction mechanism.

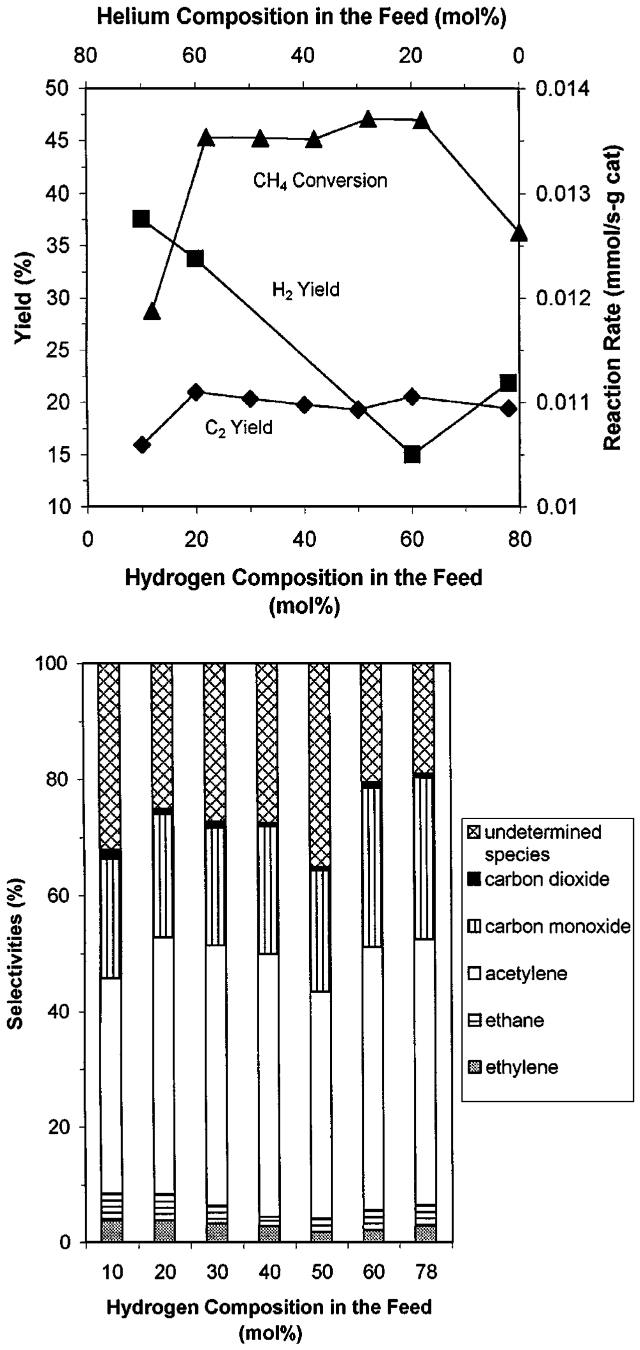

FIG. 2. Effect of hydrogen composition in the feed: (a) yields and conversions; (b) selectivities. Methane composition in the feed, 20%; oxygen additive, 2%. Overall flowrate, 25 cm^3/min; gas temperature, 373 K; input voltage, 6kV; current, 1.16 mA; input power, 6.5 W.

is acetylene (more than 85%). This supports the reaction mechanism presented in Fig. 1. The hydrogen radical is favorable to the formation of acetylene. Experiments also show that the selectivities of ethane and ethylene are always very low and there exist some undetermined carbon species, probably coke and C_3^+ hydrocarbons. Figure 2b also indicates that the hydrogen yield and the selectivity of undetermined species are reduced with increasing hydrogen feed concentration, but there is higher CO selectivity. These results suggest that CO formation is not favored under conditions of higher hydrogen yield, and the higher hydrogen feed concentrations enhance CO formation. It appears that higher hydrogen feed concentrations promote the formation of OH radicals and thereby reactions [49]–[52] are more probable.

3.3. *Effects of Oxygen*

Table 3 illustrates the effects of added oxygen on methane conversion and C_2 yield. It is seen that a small amount of oxygen added to the feed may improve C_2 hydrocarbon production. The oxygen enrichment in the gas feed reduces the C_2 selectivity but the significant increase of methane conversion offsets the selectivity decrease up to a maximum of 2% oxygen.

The reason for the increase in methane conversion with increasing oxygen is that other active species are generated in addition to hydrogen radicals when oxygen is present in CH_4/H_2 plasmas. As mentioned before, these new active species include O, oxygen anion, and OH radicals. These species are able to abstract hydrogen from methane. Table 3 also shows that hydrogen yield generally increases with increasing oxygen in the feed.

The plasma catalytic methane conversion does produce some C_3^+ hydrocarbons, including some long-chain carbonaceous substances. Some of carbonaceous species would be expected to cover the active sites of catalysts and alter the electronic processes of plasma catalytic reactions. Carbonaceous species may react with plasma species to produce hydrocarbon products. Some carbonaceous deposits will react with oxidants (oxygen and/or carbon dioxide) to form carbon monoxide. Temperature programmed oxidation (TPO) was used to characterize the carbonaceous deposits formed on the catalyst during plasma catalytic methane conversion in this study. The procedure for TPO characterization has been described elsewhere (13,17). The resultant TPO spectrum is shown in Fig. 3. Two major peaks

TABLE 3

Effect of Oxygen Addition in the Methane/Hydrogen Plasma System

Oxygen amount (mol%)	Methane conversion (%)	Selectivity				C_2 yield (%)	H_2 yield (%)
		C_2	CO	CO_2	C_{unkn}[a]		
0	18.1	76.2	0	0	23.8	13.8	24.6
1	30.2	47.2	22.5	1.3	29.0	14.2	19.6
2	33.6	38.1	40.7	3.1	18.1	13.2	28.2
4	37.9	17.4	28.9	1.3	52.4	6.5	29.4

Note. CH_4/H_2: 5/5; total flowrate: 50 cm^3/min; gas temperature: 373 K; applied power: 8.4 W; helium as diluent.

[a] unkn means undetermined carbon species.

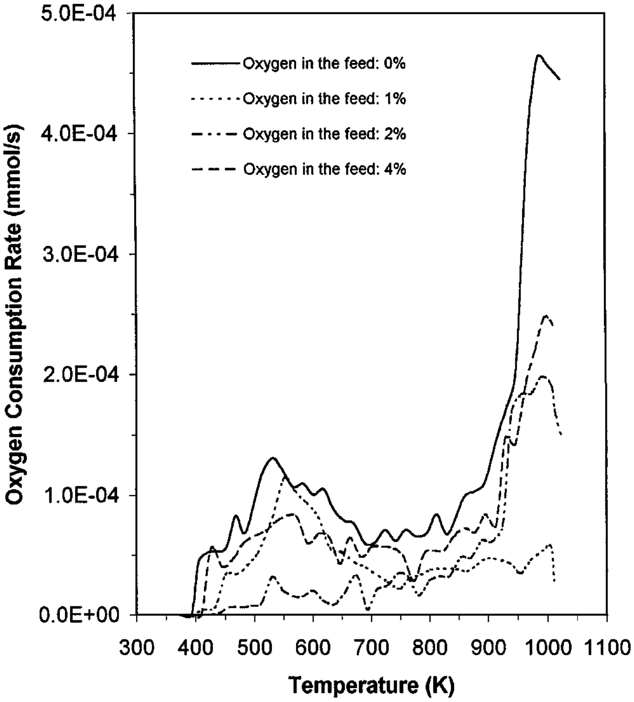

FIG. 3. TPO characterization of methane conversion over NaY using H_2 plasma with O_2 promoter. Temperature increase rate, 240 K/h; sample weight, 0.1 g (sample taken from 2-h 373 K plasma catalytic reaction); gas condition for TPO, 2.5% oxygen in helium with a total flowrate of 40 cm^3/min.

in the TPO spectrum may be seen for all of the oxygen feed concentrations. This implies that the deposited carbonaceous substances are not homogeneous. The low temperature peak (375–700 K) contains some light hydrocarbon deposits, while the high temperature peak (the peak after 700 K) indicates soot formation or some kind of more refractory carbon. The CH_4/H_2 plasma in the absence of oxygen additive results in the greatest amounts of both types of carbon. This suggests that the CH_4/H_2 plasma without oxygen produces more carbonaceous species on the catalyst surface. These results also support the explanation of polymerization occurring during the discharge reactions of CH_4/H_2 system as previously discussed. The CH_4/H_2 plasma with a small amount of oxygen (1%) produces less carbonaceous species, which can be observed from the small high temperature peak. This suggests that the large high temperature peak present in the TPO spectrum without oxygen in the feed could be some long chain species that will be oxidized in the presence of O_2. The low temperature peak of the CH_4/H_2 plasma system with 2% oxygen in the feed is small but the high temperature peak is large. This indicates that increasing oxygen in the feed reduces the low temperature peak in the TPO spectrum, which can be also observed in the CH_4/H_2 plasma system with 4% oxygen. This suggests that the low temperature peak includes some short chain species that are more readily oxidized.

3.4. Effects of the Amount of Methane in the Feed

Increasing methane in the feed induces an increase in selectivities of acetylene and undetermined carbon species, but increasing methane does not help the yields of C_2 hydrocarbons due to decreasing methane conversion, as shown in Fig. 4. As mentioned above, methyl radical formation is the

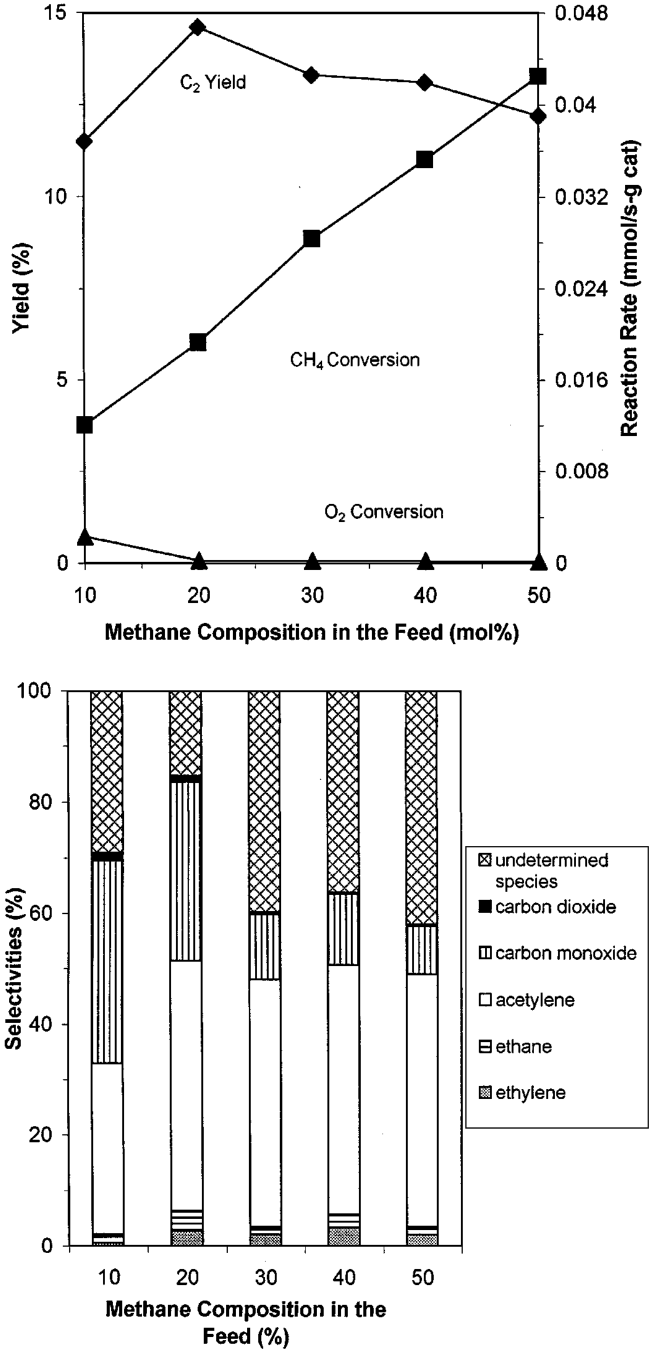

FIG. 4. Effect of methane composition in the feed: (a) yields and conversions; (b) selectivities. Hydrogen composition in the feed, 30%; oxygen additive, 2%; overall flowrate, 50 cm^3/min; gas temperature, ~70°C; input voltage, 8 kV; current, 1.22 mA; input power, 9.8 W.

rate-controlling step and higher methane concentration apparently does not increase the rate of formation of methyl radicals. This is likely due to decreases in the primary activating species from hydrogen.

3.5. *Effects of Gas Temperature*

We have previously discussed the effects of gas temperature on the corona discharges in the presence of heterogeneous catalysts (14–17). Thermodynamically, high temperatures favor the formation of C_2 hydrocarbons (reactions [5]–[7]). However, the streamer discharges which promote the desired reactions are present only at the lower gas temperatures (less than 573 K). When streamer discharges occur, it can be expected that a very active gas phase will induce much higher yields of higher hydrocarbons, thanks to the nonequilibrium characteristics of the streamer discharges. When the gas temperature is higher than 573 K, the streamer discharges disappear (the gas discharge becomes an arc-like discharge) and thermal effects will be the major factor controlling the reactions. From Fig. 5, it may be seen that the product distribution is very different in the different temperature regions. Lower temperatures favor the formation of acetylene, while no acetylene is formed at the higher temperatures (more than 573 K). This suggests that acetylene may only be formed from the nonequilibrium streamer discharges, possibly because of different plasma species generated or because the arc-like discharges present at high temperatures reduce the effective volume of gas discharges. At high temperatures in the presence of oxygen, all the oxygen is consumed even without plasmas by reacting with hydrogen to form H_2O which does not help the acetylene formation. Consequently, the maximum acetylene yield occurs at the lowest temperature tested (343 K).

3.6. *Effects of Flowrate*

The flowrate affects the residence time within the discharge zone and the catalyst bed. As shown in Fig. 6, the highest methane conversion (63.5%) with the largest yield of C_2 hydrocarbons (32.6%) has been found at the lowest flowrate tested (10 sccm; the residence time is around 2.3 s). However, longer residence times also induce higher selectivities for undetermined carbon species. The highest selectivity for acetylene (58.1%) occurs at the highest flowrate tested (100 sccm). These results suggest that the undetermined carbon species are secondary products formed from the C_2 hydrocarbons, probably acetylene. However, if oxygen is present and the residence time is sufficient, partial oxidation may lead to carbon monoxide, as shown in Fig. 6.

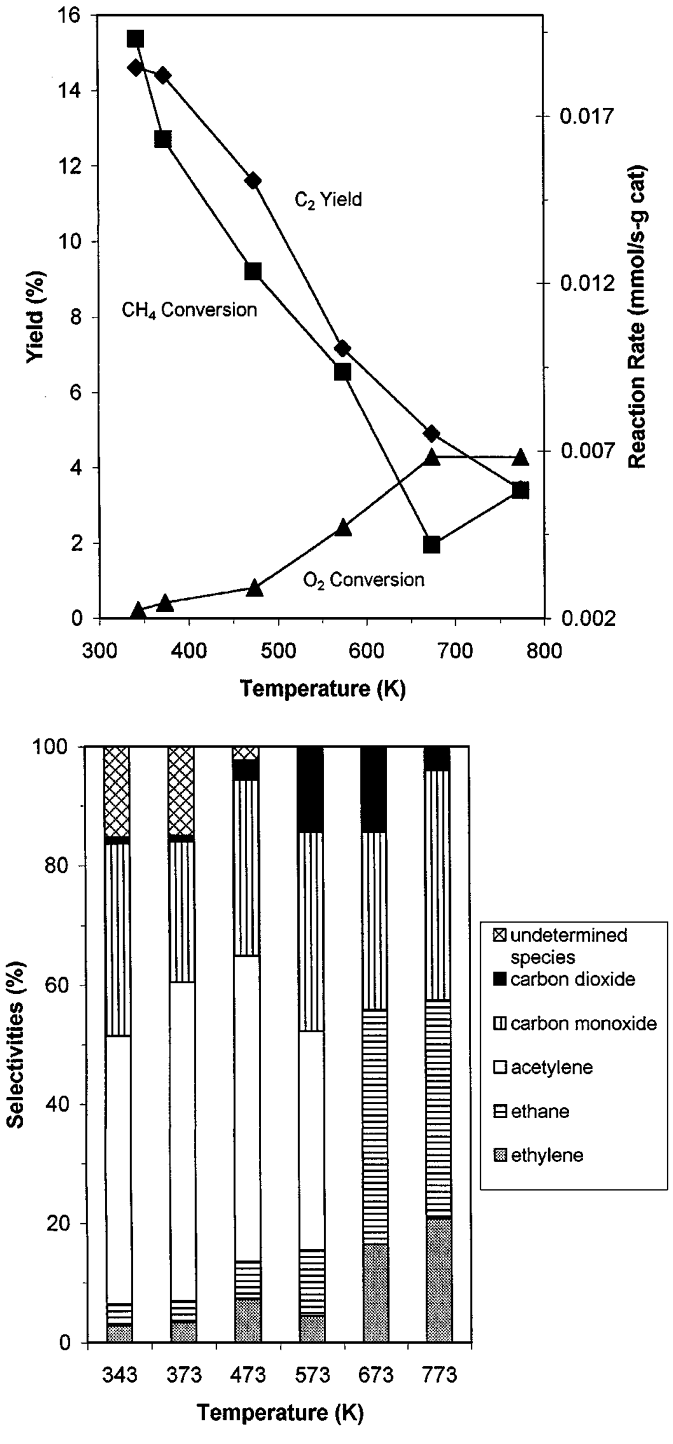

FIG. 5. Effect of gas temperature: (a) yields and conversions; (b) selectivities. Methane composition in the feed, 20%, hydrogen composition in the feed, 30%; oxygen additive, 2%; overall flowrate, 50 cm^3/min; input voltage, 8 kV; current, 1.22 mA; input power, 9.8 *w*.

4. CONCLUSIONS

The plasma catalytic production of C_2 hydrocarbons (mostly acetylene) and hydrogen over NaY zeolite has been confirmed in the present experimental study. The yields of products acetylene and hydrogen are affected by the residence time, reaction temperature, and feed composition. Because the rate-controlling step of the plasma catalytic methane conversion is methyl radical formation, improvements in this process should concentrate on ways to increase the rate of methyl radical formation without using oxygen and without leading to excessive carbon formation.

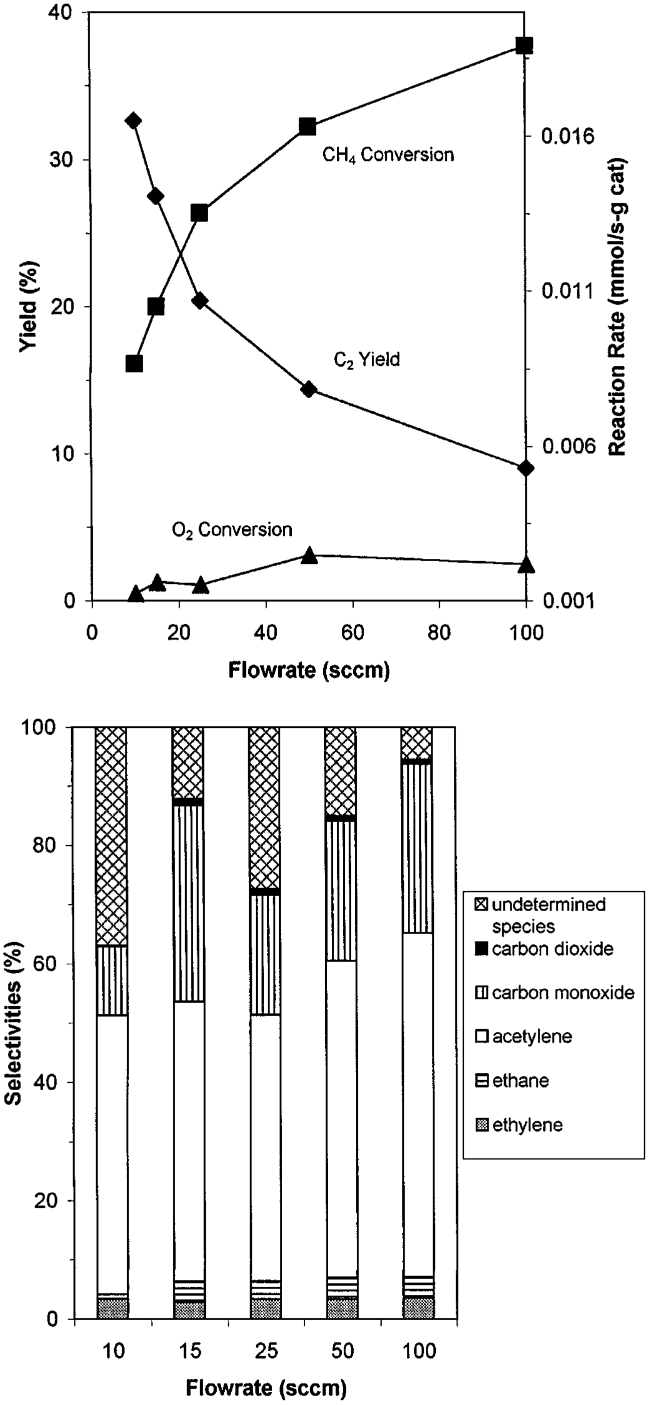

FIG. 6. Effect of flowrate: (a) yields and conversions; (b) selectivities. Methane composition in the feed, 20%; hydrogen composition in the feed, 30%; oxygen additive, 2%; gas temperature, 373 K; input voltage, 6 kV; current, 1.16 mA; input power, 6.5 W.

ACKNOWLEDGMENTS

Support from the U.S. Department of Energy (under Contract DE-FG21-94MC31170) is greatly acknowledged. The assistance from graduate students A. Marafee, C. Gordon, and P. Howard is also appreciated.

REFERENCES

1. Barbieri, G., and Di Maio, F. P., *Ind. Eng. Chem. Res.* **36**, 2121 (1997).
2. Edwards, J. H., and Maitra, A. M., *Fuel Process. Tech.* **42**, 269 (1995).
3. Holmen, A., Olsvik, O., and Rokstad, O. A., *Fuel Process. Tech.* **42**, 249 (1995).
4. Billaud, F., and Baronnet, F., *Ind. Eng. Chem. Res.* **32**, 1549 (1993).
5. Fulcheri, L., and Schwob, Y., *Int. J. Hydrogen Energy* **20**, 197 (1995).
6. Huang, J. H., and Suib, S. L., *Res. Chem. Intermed.* **20**, 133 (1994).
7. Onoe, K., Fujie, A., Yamaguchi, T., and Hatano, Y., *Fuel* **76**, 281 (1997).
8. Fedoseev, V. I., Aristov, Yu. I., Tanashev, Yu. Yu., and Parmon, V. N., *Kinet. Catal.* **37**, 808 (1996).
9. Cooney, D. O., and Xi, Z.-P., *Fuel Sci. & Tech. Int'l* **14**, 1111 (1996).
10. Anderson, J. E., and Case, L. K., *I&EC Process Design Develop.* **1**, 161 (1962).
11. Baddour, R. F., and Blanchet, J. L., *I&EC Process Design and Develop.* **3**, 258 (1964).
12. Venugopalan, M., and Veprek, S., *in* "Topics in Current Chemistry: Plasma Chemistry IV" (F. L. Boschke, Ed.), Vol. 107, p. 1. Springer-Verlag, New York, 1983.
13. Liu, C.-J., Marafee, A., Hill, B., Xu, G.-H., Mallinson, R., and Lobban, L., *Ind. Eng. Chem. Res.* **35**, 3295 (1996).
14. Marafee, A., Liu, C.-J., Hill, B., Xu, G.-H., Mallinson, R., and Lobban, L., *Ind. Eng. Chem. Res.* **36**, 632 (1997).
15. Liu, C.-J., Marafee, A., Xu, G.-H., Mallinson, R., and Lobban, L., *Appl. Catal. A* **164**, 21 (1997).
16. Liu, C.-J., Mallinson, R., and Lobban, L., *Appl. Catal. A*, in press.
17. Lobban, L., Liu, C.-J., and Mallinson, R., manuscript in preparation.
18. Oumghar, A., Legrand, J. C., Diamy, A. M., and Turillon, N., *Plasma Chem. Plasma Proc.* **15**, 87 (1995).
19. Hollahan, J. R., and Bell, A. T., "Techniques and Applications of Plasma Chemistry," Wiley, New York, 1974.
20. Meshkova, G. I., and Eremin, E. N., *Russ. J. Phys. Chem.* **44**, 255 (1970).
21. Thomas, J. K., *Chem. Rev.* **93**, 301 (1993).
22. Uchida, T., Vinogradov, G. K., and Morita, S., *J. Electrochem. Soc.* **144**, 1434 (1997).
23. Benndorf, C., Joeris, P., and Kröger, R., *Pure & Appl. Chem.* **66**, 1195 (1994).