



Comparative investigations on plasma catalytic methane conversion to higher hydrocarbons over zeolites

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Abstract

Zeolites are an important class of industrial catalyst. In this investigation, the application of zeolites for plasma catalytic methane conversion (PCMC) to higher hydrocarbons at very low gas temperatures (room temperature to 200°C) has been addressed. Zeolites NaY, HY, NaX, NaA, Linde Type 5A and Na-ZSM-5 have been tested for the application in PCMC. The products contain C₂ hydrocarbons (acetylene, ethane and ethylene), other carbon species including carbon deposits and trace C₃⁺ hydrocarbons, and syngas (H₂+CO), depending upon co-reactant or dilution gases added to the feed. A streamer corona discharge, a cold plasma phenomenon, has been found to be the most effective and efficient at inducing plasma catalytic activity over zeolites. The order of the zeolites tested from good to poor for sustaining the desired streamer discharges is NaY, NaOH treated Y > HY > NaX > NaA > Linde Type 5A > Na-ZSM-5.

Oxygen, carbon dioxide, hydrogen (with or without oxygen added in a small amount), steam and nitrogen have been tested as co-reactants or dilution gases for PCMC over zeolites. Experimental results showed that the selectivity to higher hydrocarbons decreases in the order H₂>H₂+O₂>H₂O>N₂>N₂+O₂>CO₂>O₂, while the methane conversion decreases in the order N₂+O₂>N₂>O₂>CO₂>H₂+O₂>H₂O>H₂. All the co-reactants tested here, except hydrogen, can induce high methane conversions during plasma catalytic reactions. Small amounts of oxygen added to hydrogen can improve significantly the plasma reactivity of hydrogen over zeolites. This has led to a very selective net production of hydrogen and higher hydrocarbons (especially acetylene). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the 1980s, intensive research efforts have been made to develop processes for direct conversion of methane into more valuable hydrocarbons. The

difficulty in direct methane conversion catalytically and/or thermally is the strength of the methane C–H bond, which is greater than that of the hydrocarbon products of methane conversion. High temperature operation required by direct methane conversion leads to poor economics associated with a low yield of the desired hydrocarbon products. Lower temperature methane conversions are desirable and are being

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investigated extensively [1,2]. Recently, zeolites have been found to be active for low-temperature methane conversion to more valuable hydrocarbons with and without oxidants [3–13]. Investigations on partial oxidation of methane to aromatics over zeolites have been performed by scientists in the former Soviet Union [3–5]. Several different oxidants (O_2 , N_2O , NO , NO_2 and SO_3) have been tested with different structural types of zeolites. The highest yield of higher hydrocarbons (8.4%) has been obtained in the presence of N_2O [5]. Further investigation on direct partial oxidation of methane over metal-containing ZSM-5 catalysts has also been reported [6]. Higher hydrocarbons, especially C_5^+ liquids, were produced at temperatures between 440°C and 465°C with 100% O_2 conversion. The higher hydrocarbons are believed to be formed via a methane oxidation and methanol-to-gasoline (MTG) pathway. The loaded metal serves two functions: dehydrogenation and oxidation. The yield of higher hydrocarbons achieved is 0.92% over Ga-ZSM-5, 0.13% over Pt-ZSM-5 and 1.29% over Ag-ZSM-5 zeolite [6]. The most selective product over these catalysts is carbon oxides. The selectivity of higher hydrocarbons can be improved by non-oxidative methane conversion. Wang et al. [7,8], Szöke and Solymosi [9] and Chen et al. [10] used Mo/ZSM-5 or Mo/HZSM-5-based catalysts to enhance the activity and stability for non-oxidative conversion of methane to aromatics and C_2 hydrocarbons. 100% selectivity for benzene with 7.2% methane conversion has been obtained [7]. More recently, the low-temperature non-oxidative activation of methane over H-gallosilicic acid (MFI) zeolite was reported [11]. By using alkenes as additives, a high yield of aromatics has been achieved (the highest methane conversion reported was 45% with 92% selectivity of aromatics at 600°C with *n*-butene as an additive). No methane conversion was observed without alkene additives. Further investigation of low-temperature conversion of methane over zeolites has resulted in a modification of the support (for example, its acid–base properties) by loading different metals. In this regard, Pt-loaded zeolites (Pt/NaY and Co–Pt/NaY [12]; Pt/HY and Pt/HX [13]) have been tested for a two-step non-oxidative methane conversion. CH_x species were formed during the first chemisorption step, while a series of hydrocarbons (C_1 , ethylene, ethane, C_3 , C_4 , C_5 , C_6 , and C_{7+}) were produced in the

second hydrogenation step. Co–Pt/NaY was reported to show an exceptionally high yield (100%) referred to the adsorbed CH_x species and high selectivity in the formation of C_{2+} hydrocarbons (92.6%) at 523 K for hydrogenation [12]. In general, low-temperature methane conversion over zeolites has progressed in two directions: one is the modification of the performance of support zeolite; the other is the modification of supported metal properties. Some mechanistic analyses have also been presented [7,8,10,11,14,15]. Relevant to these analyses are the properties of zeolites related to their specific electronic structures. The intensity of the natural Coulombic electric field in the zeolite microporous structure reaches 1 V/Å, which can lead to a charge-based selectivity in zeolites [16]. It is possible that the catalytic properties of a zeolite might be altered if it were electrically charged. Experimental results on methane conversion to higher hydrocarbons over electrically charged Y zeolite have been reported [17]. Such “charged” catalytic activity, obtained by the interaction of a corona discharge with a zeolite catalyst, has led to low gas temperature methane conversion. No higher hydrocarbons activity was observed over this catalyst in the absence of corona discharge at any temperature (up to 1000 K). The catalytic properties of the zeolite are clearly modified by the gas discharges. It is generally accepted that the thermal-catalytic oxidative coupling of methane involves both heterogeneous and homogeneous reactions. The activation of methane by catalyst active sites at high temperatures results in the formation of methyl radicals that react homogeneously to form ethane. When a plasma, usually cold plasma, is generated in proximity to or within a catalyst layer or catalyst bed, both heterogeneous and homogeneous reactions will be affected. In this paper, a comparative investigation on plasma catalytic methane conversion to high hydrocarbons over different kind of zeolites is presented. The effects of various co-reactants on this conversion will also be described.

2. Experimental

2.1. Apparatus

The experimental apparatus has been previously described [17,18]. The reactor was made of a quartz

tube with an ID of 7.0 mm. The reactor was heated by a cylindrical furnace placed around the reactor. When a lower gas temperature was desired for the plasma catalytic reactions, the reactor exterior was cooled by flowing room air. An Omega K-type thermocouple was attached to the outside wall of the reactor to monitor and control the reactive gas temperature. The temperature measured in this way was calibrated with the temperature inside the reactor tube and has been discussed elsewhere [17,18]. All the experiments were conducted at atmospheric pressure. The feed gas flow rates were regulated by mass flow controllers (Porter Instrument, Model 201). The feed gases were well mixed and then introduced downward through the reactor for all the experiments. The feed was analyzed by an on-line gas chromatograph (HP5890) with a thermal conductivity detector (TCD). The exhaust gas from the reactor was introduced into a condenser to remove water, and then analyzed by the HP gas chromatograph. A CARLE series 400 AGC (EG & G) was used for the detection of hydrogen and C₃⁺ hydrocarbons produced.

2.2. Corona discharge

A dc corona discharge, which is a cold plasma phenomenon, was used in this research on PCMC. In the present reactor design, a wire and plate electrode configuration is used. The reactor and electrode configuration have been described previously [17,18]. The gas discharges are formed in a gap between the stainless steel electrodes. The upper wire electrode is concentric with the reactor tube, while the lower electrode is circular with holes for gas flow and is positioned perpendicular to the reactor axis and 10 mm below the tip of the wire electrode. The dc corona discharge is created using a high voltage power supply (Model 210-50R, Bertan Associates). The lower plate electrode is always held at a potential

of 0 V (i.e., grounded). The catalyst bed (0.1 g of catalyst in powder form) is held on the lower plate electrode, and thus is between the electrodes.

2.3. Catalysts and catalyst characterization

The zeolite catalysts tested in this work include NaY, NaOH treated Y, HY, NaA, NaX, Na-ZSM-5 and Linde type 5A zeolite. The NaY, NaA and NaX zeolites were obtained from Aldrich, HY from UOP, Na-ZSM-5 from Chemie Uetikon, and Linde type 5A zeolite from Matheson, Coleman and Bell. All these zeolites were used as received. The composition and pore diameters of all these zeolites are shown in Table 1 [19]. NaOH treated Y zeolite was prepared by NaOH treatment of the commercial NH₄Y zeolite (Aldrich), which has been discussed elsewhere [17]. The objective of NaOH treatment is to dissolve part of the Si to increase the catalyst's polarizability [20] and basicity. After such treatment, a significant decrease in surface Si/Al was found by using XPS characterization [17]. X-ray diffraction (XRD) was used to identify the solid-state phases of NH₄Y zeolite before and after NaOH treatment. The XRD characterization was performed on a D/max-γA instrument run at 40 kV and 40 mA with filtered Cu K_α radiation (λ=0.1541 nm). The XRD spectra of NH₄Y zeolite before and after NaOH treatment, of NaOH treated NH₄Y after plasma reaction, and of NaY zeolite as received from Aldrich, all show the faujasite structure, indicating that neither the NaOH treatment nor the PCMC reactions change the phase state of the zeolite.

Table 2 presents crystal size of zeolites obtained from XRD measurements. The NaOH treatment of NH₄Y apparently increases the crystal size of the zeolite, while the plasma reactions may slightly decrease the crystal size. Thermogravimetric analysis (TGA) was also carried out using a Shimadzu TGA-50 instrument to characterize the dehydration perfor-

Table 1
Composition and pore diameters of some of the zeolites used [19]

Type	Unit cell composition	Void volume (ml/ml)	Pore diameter (Å)	Si/Al ratio
NaA	Na ₁₂ (AlO ₂) ₁₂ (SiO ₂) ₁₂	0.47	4.2	1
NaX	Na ₈₆ (AlO ₂) ₈₆ (SiO ₂) ₁₀₆	0.50	7.4	1.23
NaY	Na ₅₆ (AlO ₂) ₅₆ (SiO ₂) ₁₃₆	0.48	7.4	2.43
Na-ZSM-5	(Li,Na) ₂ (AlO ₂) ₂ (SiO ₂) _{3.2m}	0.53	–	>10

Table 2
Crystal size of zeolites

Zeolite	Crystal size (Å)
NH ₄ Y from Aldrich	1078
NaOH treated NH ₄ Y	1212
NaOH treated NH ₄ Y, after plasma reactions with oxygen as a co-reactant	1182
NaY from Aldrich	1617

mance of zeolites. During TGA experiments, the sample was heated under vacuum at a rate of 10°C/min and the loss of sample weight due to dehydration was recorded.

2.4. Co-reactants

The co-reactant has an important influence on the selectivities in plasma catalytic methane conversion. In this investigation, oxygen, nitrogen, hydrogen, steam and carbon dioxide have been investigated as co-reactants. To compare the plasma catalytic reactivity among different zeolites, only the oxygen results were used because of the greater discharge stability achievable when using oxygen due to oxidation of carbonaceous deposits. All the plasma catalytic reactions conducted in this work used helium as a dilution gas.

3. Results and discussion

3.1. Gas temperature effect

As mentioned elsewhere [17,18], the zeolites used in this investigation showed no activity for methane conversion to higher hydrocarbons (only CO and CO₂ were observed as products) in the absence of gas discharges up to 750°C. To start the plasma catalytic reactions, a high positive voltage was applied to the wire electrode. When the voltage is sufficiently high, gas discharges develop through the catalyst bed. The effect of gas temperature on the types of corona discharges in the presence of heterogeneous catalyst has been previously discussed [17,18]. Good plasma catalytic activity was achieved only when streamer discharges [21] were present. The streamer discharges were present only at gas temperatures below that at

which extensive dehydration occurred. At higher temperatures, the streamer discharge turns to an arc-like discharge and thermal effects dominate the reactions. The order of the zeolites tested from easy to difficult for achieving streamer discharges is

NaY, NaOH treated Y > HY > NaX > NaA
> Linde Type 5A > Na-ZSM-5.

The last two zeolites require very low temperatures (~50°C or less) to sustain the streamer discharges. When streamer discharges occur, a plasma phase is obtained that induces much higher yields of radical species and, we believe, leads to more charges attached to the catalyst, compared to non-streamer discharges. Fig. 1 shows the TGA results of Na-ZSM-5 and NaOH treated Y zeolite. It is clear that the dehydration occurs very quickly at the beginning

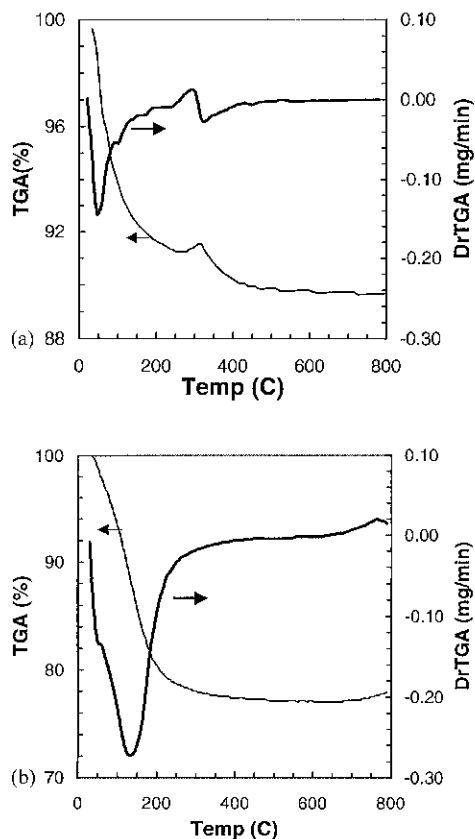


Fig. 1. TGA curves during heating under vacuum of (a) Na-ZSM-5 and (b) NaOH treated NH₄Y.

(before 50°C) for both Na-ZSM-5 and NaOH treated Y. However, when the temperature reaches around 47°C, the dehydration rate of Na-ZSM-5 decreases, while the dehydration rate of NaOH treated Y zeolite still increases until 134°C. These results indicate a much wider temperature range for dehydration of NaOH treated Y zeolite, compared to Na-ZSM-5. This means that the moisture amount and/or the amount of OH groups is much greater in NaOH treated Y than in Na-ZSM-5 for temperatures above 50°C. The dehydration temperature range showed in the TGA measurements corresponds to the temperatures at which streamer discharges can be sustained with resulting good plasma catalytic activity for methane conversion. These results support the hypothesis that OH groups (Brønsted sites) are important to PCMC [17]. The effects of temperature on PCMC over NaOH treated Y zeolite have been discussed elsewhere [17]. Fig. 2 shows a similar experimental result of temperature effects on plasma catalytic oxidative conversion of methane over HY zeolite. The products include C₂ hydrocarbons (acetylene, ethylene and ethane), undetermined carbon species including deposited carbon and trace C₃⁺ hydrocarbons, trace formaldehyde, syngas (H₂+CO) and carbon dioxide. The product distribution changes significantly with temperature. Low temperature favors the formation of the undetermined carbon species. At higher temperatures (more than 400°C), the selectivity for the undetermined carbon species is reduced significantly, while CO₂ selectivity increases quickly. This suggests different primary pathways at different temperatures. The non-equilibrium streamer discharge present at lower temperatures favors the formation of higher hydrocarbons. It is also well known that the electron attachment to carbon dioxide occurs in streamer discharges [21,22]:



Reactions (1) and (2) may explain the low selectivity for carbon dioxide at low temperatures, while O⁻ and other oxygen species formed from these reactions may provide more active species for methane conversion. The electron attachment reaction of carbon dioxide may also explain the increase in selectivities of CO and C₃⁺ (with the other undetermined carbon species) at low temperatures. At higher

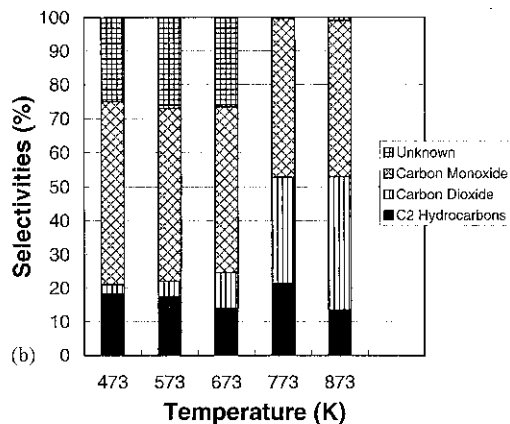
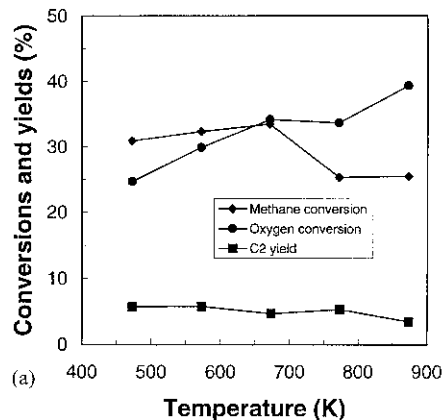


Fig. 2. Effect of gas temperature over HY zeolite: (a) yield and conversions; (b) selectivities. Methane composition in the feed: 20%; oxygen composition in the feed: 10%; total flow rate: 100 cm³/min; applied voltage: 7 kV; applied power: 7.84 W; catalyst weight: 0.1 g.

temperatures, the gas discharge shifts to an arc-like discharge which reduces the effective reaction region because the arc is much more localized than the streamers. The arc discharge reduces the selectivity for higher hydrocarbons and more carbon dioxide is produced.

3.2. Plasma catalytic oxidative conversion of methane over different zeolites

A mechanism for plasma catalytic oxidative conversion of methane has been discussed elsewhere [17]. The specific oxygen species thought to be responsible for methane radical formation are O⁻ [23] and O (¹D)

in gas discharges containing oxygen [24,25]. PCMC over zeolites is assumed to occur by a combined homogeneous and heterogeneous mechanism. It is proposed that methane activation is through interaction with electronically excited species and polarized Brønsted acid sites on the zeolites [17]. Oxygen has an important role not only in the supply of active species for the activation of methane but also in the stabilization of the streamer discharge. However, oxygen also has a negative effect on the formation of higher hydrocarbons because the newly formed hydrocarbons are still in excited states and may easily react with oxygen to be oxidized. Fig. 3 shows that the selectiv-

ities to higher hydrocarbons decrease with the increasing oxygen partial pressure, while the selectivities for carbon oxides increase. The selectivities for higher hydrocarbons can be improved by replacement of oxygen with other oxidants or co-reactants in the role of methane “activator” as discussed later.

Table 3 presents the experimental results of PCMC over the different zeolites. Table 3 shows that NaX, NaA and NaOH treated Y lead to more significant methane conversions, compared to Linde Type 5A and Na-ZSM-5. The zeolites most selective for higher hydrocarbon formation are NaOH treated Y and NaX. The lowest selectivity for higher hydrocarbons is obtained with Linde Type 5A. This ordering of activity appears to be related to hydrated electrons and acid–base property of zeolites, which will be discussed in detail in another paper [26].

Among these zeolites, the NaOH treated Y has the highest density of basic sites and NaX has the strongest basic sites, while Na-ZSM-5 is the most acidic. It is clear from Table 3 that strong acid sites lead to a poor PCMC activity. It was found that significant carbonaceous deposits during plasma catalytic reactions over Na-ZSM-5 were produced so that the catalyst deactivated quickly. The experiments have also shown that the carbonaceous deposits on Na-ZSM-5 will shift the streamer discharge to an arc-like discharge and reduce the plasma activity, while the carbonaceous species formed on the other zeolites do not have such negative effect. The carbonaceous deposits on different zeolites will be analyzed by the temperature-programmed oxidation and will be discussed later [28].

It should be noted that there are several possible interactions between the discharge, gas species, and catalyst. The discharge occurring in the volume above the catalyst bed certainly changes the gas composition flowing over the catalyst (compared to the gas composition in the absence of the discharge) by creation of intermediate species. The difference in product composition between the two cases is probably partly due to the interaction of these intermediate species with the catalyst surface. Furthermore, the discharge characteristics (and, therefore, the intermediate species) are strongly influenced by the surface properties of the catalyst. As noted, carbon deposition on the surface has a pronounced effect on the discharge. In addition, the discharge and/or presence of charged species might

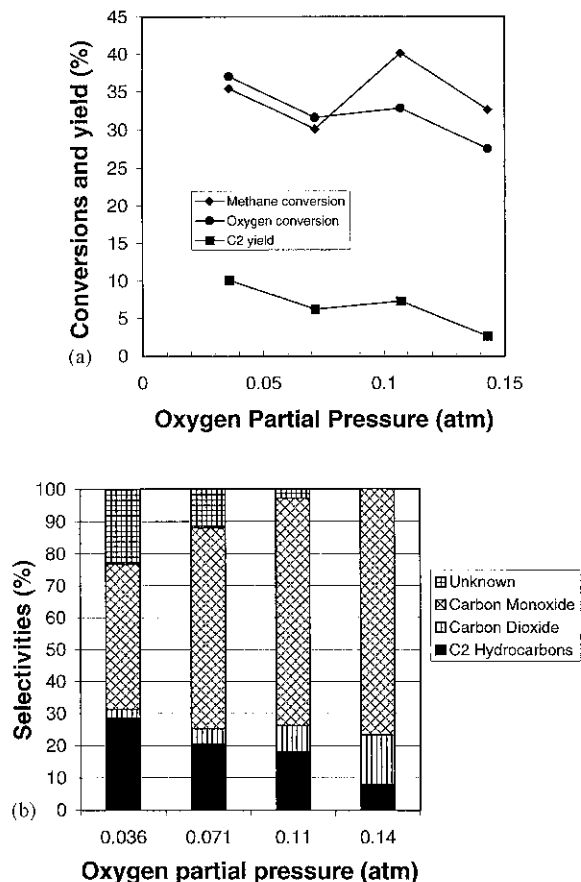


Fig. 3. Effect of oxygen partial pressure on plasma catalytic methane conversion over NaOH treated Y zeolite: (a) yield and conversions; (b) selectivities. Gas temperature: 200°C; total flow rate: 70 cm³/min; applied voltage: 6 kV; applied power: 7 W; methane partial pressure in the feed: 0.14 atm; catalyst weight: 0.1 g.

Table 3
Experimental results of plasma catalytic methane conversion over zeolites^a

Zeolite	Flow rate (sccm)	CH ₄ /O ₂	Applied power (W)	Gas temperature (°C)	CH ₄ conversion (%)	O ₂ conversion (%)	C ₂ selectivity (%)	C _{unkn} ^b selectivity (%)	CO selectivity (%)
NaX	25	4/1	8.4	50	48.1	46.6	33.7	27.4	37.3
NaX	50	4/1	8.4	50	33.2	28.4	34.9	29.8	33.7
NaA	25	4/1	8.4	50	49.0	41.2	24.8	27.2	45.6
NaA	50	4/1	8.4	50	31.5	26.0	29.4	28.5	40.2
Linde 5A	25	4/1	8.4	50	39.9	38.3	27.6	0.62	69.0
Na-ZSM-5 ^c	25	4/1	11.3	50	44.6	47.5	31.2	15.5	51.5
NaOH treated Y	25	4/1	8.4	50	50.0	39.5	25.0	36.9	36.5
NaOH treated Y	50	2/1	7.8	200	30.1	31.6	20.6	12.0	62.7
NaY (Aldrich)	50	2/1	8.4	150	37.4	28.1	17.3	35.8	43.8

^aAll results were obtained from more than 2 h experiments except Na-ZSM-5.

^bunkn means the undetermined carbon species including C₃⁺ hydrocarbons.

^cThe result presented here is from the first half hour before the catalyst was covered with carbonaceous deposits.

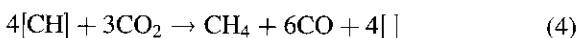
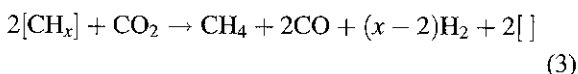
alter the surface properties of the catalyst, modifying the surface catalytic properties. However, we have as yet been unable to show which of these effects are the most significant for methane conversion.

3.3. Effect of co-reactants

Oxygen is very effective for low gas temperature plasma activation of methane by the interaction between the plasma and catalyst. However, oxygen can also induce an oxidation of hydrocarbons, which reduces the yield of desired products, as shown in Fig. 3. In this investigation, carbon dioxide, hydrogen, nitrogen and steam have been tested as co-reactants for plasma catalytic methane conversion to higher hydrocarbons.

3.3.1. Carbon dioxide

It has already been mentioned that the dissociation or dissociative attachment of carbon dioxide (reactions (1) and (2)) will generate active species that assist plasma catalytic methane conversion. Carbon dioxide, as an oxidant, is also very effective in the inhibition of carbonaceous deposits formed during plasma catalytic reactions evidently through [27]:



Experiments for plasma catalytic methane conversion using CO₂ as an oxidant confirm a significant methane conversion over NaOH treated Y zeolite. The products include acetylene, ethylene, ethane, syngas (CO+H₂), C₃⁺ species (propane, *n*-butane, isobutane, 1-butene, *n*-pentane, C₆⁺) together with some other unknown materials. The experiments show a significant yield of unknown species (including some C₃⁺ hydrocarbons) during the PCMC over NaOH treated Y zeolite. The distribution of hydrocarbon products changes significantly with the CH₄/CO₂ feed ratio, as shown in Table 4. The selectivity for unknown species decreases with increasing CH₄/CO₂ ratio, while the selectivity for CO and the H₂/CO ratio in the syngas increase with increasing CH₄/CO₂. These trends suggest that the unknown species could be formed from secondary CO₂ reactions. Lower amounts of CO₂ in the feed favor the production of C₂ hydrocarbons. Table 4 also suggests that lower gas temperatures give higher C₂ yields with larger H₂/CO ratios.

3.3.2. Hydrogen

Methane radicals can be generated from reactions with H radicals during PCMC reactions:



It can be expected that 100% selectivity for higher hydrocarbons will be achieved if hydrogen alone is supplied as a co-reactant for PCMC. Hydrogen

Table 4
Effect of CH₄/CO₂ feed ratio and gas temperature on PCMC

CH ₄ /CO ₂ in feed	Temperature (°C)	X _{CH₄} (%)	X _{CO₂} (%)	Selectivities					Yield		H ₂ /CO ratio
				C ₂ H ₄	C ₂ H ₆	C ₂ H ₂	C _{unkn}	CO	C ₂	C _{unkn}	
1/3	200	41.9	17.1	1.6	2.1	7.6	85.3	3.4	4.71	35.74	0.86
1/2	200	52.3	16.3	1.4	1.7	8.5	80.6	7.8	6.07	42.16	1.25
1/1	200	56.3	22.8	1.9	1.8	15.0	72.2	9.1	10.54	40.65	2.12
1/0.5	200	45.0	21.7	3.3	2.4	25.5	58.3	10.5	14.08	26.24	3.55
1/0.5	100	44.4	22.8	1.7	1.7	28.8	57.2	10.6	14.35	25.40	3.75
1/0.5	35	45.3	22.0	2.3	2.7	29.4	54.8	10.8	15.46	24.82	4.12

Total flow rate: 25 sccm; CH₄ feed partial pressure: 0.2 atm; catalyst weight: 0.1 g; input power: 8.4 W; applied voltage: 7 kV.

radicals may be easily generated in corona discharges and these radicals can react rapidly with zeolite-adsorbed CH_x species to produce higher hydrocarbons. However, under these conditions the experiments showed low yields of higher hydrocarbons due to deactivation of the catalyst. This is evidently due to the polymerization that occurs during the discharge reactions and that binds catalyst particles together and covers the surface and pores. To prevent polymerization within the zeolite, as well as to sustain the streamer gas discharge, a small flow of oxygen was added to the feed. Some active species (O, O⁻ and OH) will be generated from the oxygen. These radicals are strong bases and possess strong H-atom affinity, enabling them to have an exothermic H-atom abstraction reaction with hydrocarbons or carbonaceous deposits containing C–H bonds. By adding the oxygen, the streamer discharges were sustained and high yields of higher hydrocarbons have been achieved, as shown in Table 5. Table 5 shows very selective production of higher hydrocarbons, especially at lower flow rates. This could lead PCMC to a practical level for the production of ethylene, acetylene and hydrogen.

3.3.3. Steam

Steam, with its two hydrogen atoms and one oxygen atom, is very attractive to be developed as a co-reactant for PCMC. H and OH can be generated from steam during gas discharge reactions:



Table 5

Experimental results of plasma catalytic methane conversion using hydrogen as a co-reactant over NaOH treated Y zeolite (catalyst weight: 0.1 g)

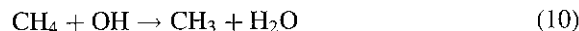
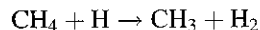
CH ₄ /H ₂ /O ₂	10/15/1	10/15/1	10/15/1
Flow rate (sccm)	10	25	50
Residence time (s)	2.3	0.9	0.46
Gas temperature (°C)	100	100	100
Applied voltage (kV)	6	6	6
Applied power (W)	6.5	6.5	6.5
Selectivity of C ₂ (%)	51.2	51.3	60.3
Yield of C ₂ (%)	32.6	20.4	14.4
Selectivity of C _{unkn} (%)	36.9	27.3	15.1
Yield of C _{unkn} (%)	23.4	10.8	5.6
Selectivity of CO (%)	11.7	20.3	23.5
Selectivity of CO ₂ (%)	0.2	1.1	1.1
Yield of H ₂ (%) ^a	49.6	46.5	54.4
H ₂ /CO	9.7	7.3	7.2
Methane conversion (%)	63.5	39.7	23.9

^a 0.5 × (moles H₂ formed/moles CH₄ fed) × 100%

Some active oxygen species will be further generated from OH:



All these radicals, H, OH and O, possess a potential for abstracting a hydrogen from methane to form methyl radicals and initiate methane conversion:



The radicals OH and O generated from steam are very effective and efficient in the inhibition of carbon deposits on the catalyst [17,29] to sustain the streamer

Table 6
Experimental results of plasma catalytic methane conversion using steam as a co-reactant over NaOH treated Y zeolite

CH ₄ /H ₂ O	0.71/1	1.56/1	1.09/1	2.18/1	1.27/1
Flow rate (sccm)	10	25	45	50	105
Residence times (s)	2.3	0.9	0.51	0.46	0.21
Gas temperature (°C)	~130	~90	~100	~100	~100
Applied voltage (kV)	7.5	7.5	4	6	6
Applied power (W)	9.0	9.0	4.3	7.0	6.8
Selectivity of C ₂ (%)	17.5	27.0	51.8	55.9	49.2
Yield of C ₂ (%)	9.5	12.5	13.7	16.1	5.5
Selectivity of C _{unkn} (%)	52.6	41.2	0	8.6	2.5
Yield of C _{unkn} (%)	28.7	19.0	0	2.2	0.28
Selectivity of CO (%)	28.2	31.8	48.2	35.5	48.3
Selectivity of CO ₂ (%)	1.7	0	0	0	0
H ₂ /CO	2.5	3.2	4.4	7.2	4.3
Methane conversion (%)	54.5	46.1	26.5	25.3	11.1

corona discharges. The apparatus and procedures for adding H₂O into the gas feed have been described elsewhere [30].

The PCMC using steam as a co-reactant was conducted at ~100°C. Table 6 shows the experimental results obtained. Little or no carbon deposition or C₃⁺ hydrocarbon formation occurs with steam as a co-reactant when the total flow rate is sufficiently high. A major product at high flow rates (>45 cm³/min) is syngas. The other selective product is C₂ hydrocarbons and the yield of C₂ is slightly better than that obtained using H₂ as a co-reactant. At lower flow rates (higher residence times), more carbon deposition occurs (along with trace C₃⁺ hydrocarbon formation). The yields of C₂ hydrocarbons and syngas were reduced. It is clear that the H₂/CO ratio of the syngas decreases at lower flow rates. These results suggest some Fischer–Tropsch synthesis may occur during PCMC reactions at lower flow rates. Since steam is a much cheaper co-reactant compared to hydrogen, there is a significant potential to develop PCMC to selectively produce C₂ hydrocarbons and syngas using steam as a co-reactant and/or oxidant at suitable flow rates.

3.3.4. Nitrogen

The methane radical reactions with nitrogen have been well studied with methane conversion via microwave discharge [24,31]. It is also well known that molecular nitrogen subjected to the action of gas discharges is chemically reactive. This reactivity is mainly due to vibrationally excited molecules in the

ground electronic state ($X^1\Sigma_g^+, \nu$), electronically excited molecules in metastable states ($A^3\Sigma_u^+$), ($\alpha^1\Sigma_u^-$), ($\alpha^1\Pi_g$), and N atoms in the ground state (4S) or in the metastable states (2D) or (2P) [24,31]. As an abundant and inexpensive source, nitrogen could be a good co-reactant for activation of methane in PCMC. A significant problem is that some by-products may contain -CN groups or other organo-nitrogen moieties. However, this problem has not been significant under microwave discharge [24,31]. Since the corona discharge used here is a relatively low energy plasma phenomenon compared to microwave discharge, nitrogen conversion should not be a problem for PCMC over zeolites when using nitrogen as a co-reactant.

Fig. 4 shows the effect of feed oxygen and nitrogen partial pressures on PCMC using a gas mixture of nitrogen and oxygen as a co-reactant. The total flow rate of the feed gas is 25 cm³/min. Fig. 4 shows a significant methane conversion within the whole range of oxygen and nitrogen partial pressures. The C₂ selectivity and C₂ yield increase with the increasing nitrogen partial pressure and/or with the decreasing oxygen partial pressure. Further investigation is needed to identify any organo-nitrogen and NO_x species generated.

4. Conclusions

All the zeolites tested in this investigation showed significant PCMC activity. The importance of strea-

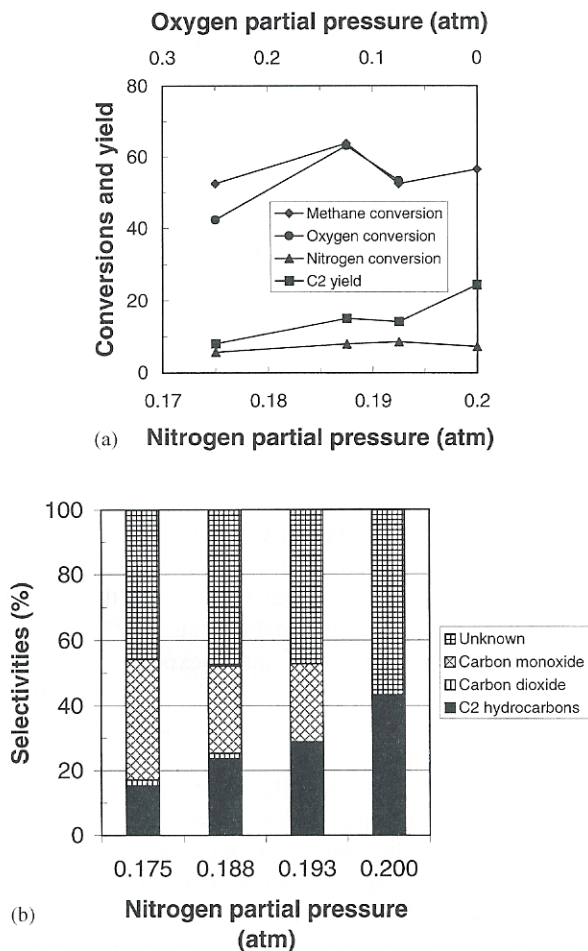


Fig. 4. Effect of nitrogen partial pressure on plasma catalytic methane conversion over NaOH treated Y zeolite: (a) yield and conversions; (b) selectivities. Gas temperature: 100°C; total flow rate: 25 cm³/min; applied voltage: 9 kV; applied power: 11 W; methane partial pressure in the feed: 0.2 atm; catalyst weight: 0.1 g.

mer versus arc discharges during plasma catalytic reactions has been shown. NaY, NaA, NaX and Linde Type 5A possess the ability to sustain such streamer discharges but Linde Type 5A has poor reactivity. Due to its strongly acidic nature, Na-ZSM-5 generally leads to carbonaceous deposits and does not appear to be suitable for PCMC. The comparative study of the effect of co-reactants on PCMC suggests that hydrogen (with oxygen additive) may be the best choice for high methane conversion with good selectivity for hydrogen and higher hydrocarbon products. Steam

is also an inexpensive co-reactant if C₂ hydrocarbon and syngas are the product objectives.

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