

Experimental Investigations on the Interaction between Plasmas and Catalyst for Plasma Catalytic Methane Conversion (PCMC) over Zeolites

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ABSTRACT

In this study, temperature programmed CO₂ desorption, a two-step plasma catalytic methane conversion (PCMC), and temperature programmed oxidation of carbonaceous species were carried out to investigate the interactions between the plasma and heterogeneous catalysts. The experiments demonstrated that NaOH treated Y, NaY and NaX zeolites, which have significant basicity, stabilize sustained streamer corona discharges at low temperatures leading to better and longer lived PCMC. The experiments also confirmed that the basicity, polarity and reactivity of zeolites may be increased by the plasma leading to improved behavior for PCMC. TPO of carbonaceous deposits show that NaX, NaY, NaA and 5A zeolites generate less coke and it is oxidized below about 650 K, while NaZSM-5 generates significantly more coke which oxidizes at higher temperature. This more refractory coke appears to destabilize the plasma leading to arcing and poorer PCMC performance. A two-step PCMC in which methane is adsorbed without plasma and then the plasma is generated with co-reactants but without methane in the gas phase showed that active plasma species interacting with the catalyst surface are necessary for the selective production of higher hydrocarbons.

1. INTRODUCTION

Plasma chemical processing is a promising route for the synthesis of chemicals, for the cleanup of waste streams, and for the modification of material surfaces. Many kinds of reactive particles, electrons, free radicals, ions, metastable species and photons, are produced in a plasma chemical processing system. Among all of the plasma generated species, free radicals are believed to be most important for chemical reactions. Control and manipulation of free radical reactions are therefore essential for the successful application of plasmas for organic synthesis [1]. However, the electrons within plasmas serve principally to excite and decompose the gas molecules at a high rate but in a non-selective fashion. Multi-pathway chemical reaction mechanisms may therefore not be avoidable and lead to production of complex product distributions.

One way to surmount this difficulty is to introduce a heterogeneous catalyst into the plasma [2-16]. Reactions combining a low temperature, non-equilibrium plasma and catalyst can be carried out at very low gas temperatures which inhibit the formation of by-products which occur at high temperatures. Such a combination has led to products that are very difficult or very expensive to achieve by regular thermal-catalytic technologies [4].

PCMC with zeolites achieving yields up to 32 percent over zeolites has recently been reported [17]. The structure of the zeolite was shown to have a significant impact on the activity and longevity of PCMC, but the reasons for these variations were not evident. In this paper, results of an experimental investigation of the interactions between plasma and catalyst for PCMC to higher hydrocarbons over

zeolites is reported.

2. EXPERIMENTAL

2.1. Reactor System

The activity for plasma catalytic methane conversion over all of these zeolites has been previously reported and a detailed description of the plasma catalytic micro-reactor system can be found elsewhere [5,8,17]. The reactor is a quartz tube with an inside diameter of 7.0 mm. A lower plate electrode is mounted perpendicular to the tube axis with holes in it to allow gas flow. Catalysts are supported on this electrode. The upper electrode is a wire suspended above the catalyst bed and the distance between the electrodes is 10 mm. The discharge is created by a Bertan Associates Model 210-50R high voltage dc power supply with the lower electrode as the ground. An oven surrounds the reactor tube to provide controlled temperatures when needed. Gas flows are established by Porter Instruments mass flow controllers and calibrated with a bubble meter.

2.2. Catalysts

The zeolite catalysts used in this work include NaX, Na-ZSM-5, NaY, NaA, Linde type 5A zeolite and NaOH treated NH_4Y zeolite. The NaY, NaA, NaX and NH_4Y were obtained from Aldrich and the first three zeolites were used as received. The Na-ZSM-5 was obtained from Chemie Uetikon, and Linde type 5A from Matheson Coleman and Bell. Both of these two zeolites were also used as received. The NaOH treatment of NH_4Y zeolite has been discussed elsewhere [8,17].

2.3. CO_2 Temperature Programmed Desorption (TPD)

Temperature Programmed Desorption (TPD) was performed with a tubular temperature-programmable plasma catalytic reactor. The reactor system is the same as the plasma catalytic micro-reactor system mentioned above. Helium at 200 ml/min was supplied to the reactor at 200°C for two hours to desorb any contaminants from the surface of the catalyst before TPD characterization. The catalyst was then cooled to 50°C or heated up to 500°C for CO_2 chemisorption in 8% CO_2 /helium at a total flowrate of 25 ml/min. A gas chromatograph (HP5890) with a thermal conductivity detector (TCD) was used to detect the CO_2 in the effluent. The CO_2 chemisorption was not terminated until a constant CO_2 level was observed in the effluent. The system was then cooled down quickly to room temperature by flowing compressed air between the furnace and the outer quartz reactor. Helium at 200 ml/min was supplied to the reactor again to purge out any gaseous CO_2 residue before the TPD measurement was started. During the TPD characterizations, the heating rate was 7.5 °C/min and helium flow rate was 20 ml/min for desorption. The maximum temperature was typically 750°C. The GC was also used to measure the desorbing CO_2 .

2.4. Temperature Programmed Oxidation (TPO)

PCMC can cause coke formation on the catalyst surface. Information about the carbonaceous species which have formed during PCMC is helpful towards understanding the mechanism of the plasma-heterogeneous reactions. It has been found experimentally that some carbonaceous species have little effect on plasma reactions, while some have a significant negative effect. TPO can give information about the nature of the carbonaceous species on the catalysts. The setup for TPO is the same as for TPD described above. The procedure for TPO is:

- a. 200 ml/min helium is used to purge the zeolite for two hours at 200°C;
- b. The system is cooled down to the desired temperature for plasma catalytic reactions;
- c. Plasma reactions are conducted for two hours or more at 50°C;
- d. The plasma is stopped and the reactor is quickly cooled down to room temperature;
- e. 200 ml/min helium is used to purge residual gases from the system;

f. The TPO experiment is begun at room temperature with 33.3% oxygen in helium with a total flow of 20 ml/min. The temperature increase rate is also 7.5°C per minute.

2.5. Two-step PCMC for the Investigation of the plasma surface reactions

To investigate the plasma surface reactions of chemisorbed methane, a two-step plasma catalytic methane conversion was conducted. In the first step, methane chemisorption without plasma was performed at 250°C with 5% CH₄/helium with a total flow of 100 ml/min over NaY zeolite. 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 minutes [18] in a separate experiment. To accomplish this, helium (200 ml/min) was flowed first to purge any non-chemisorbed methane. During the oxidation, the carbon dioxide which was formed was adsorbed in a molecular sieve column. The amount of carbon dioxide collected on the molecular sieve was then determined by running a TPD measurement, as described above. In the second step, a 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 by the HP5890 GC with TCD detector.

3. RESULTS AND DISCUSSION

Previous results for PCMC have demonstrated different plasma catalytic activities for methane conversion to higher hydrocarbons with different zeolites [17]. The highest methane conversion has been achieved over NaOH treated Y zeolite, while the best selectivity for C₂ hydrocarbon products was obtained with NaX zeolite. A difference between these two zeolites is their base properties [19,20,21]. Both hydroxyl groups and oxygen ions of (AlO₄) tetrahedra contribute to the total basicities of zeolites, whereas the latter exhibit Lewis basicity alone [19]. In this work, CO₂ TPD was used to characterize the base properties and plasma effects on these properties because of the difficulty in using conventional characterization techniques in the presence of a plasma. CO₂ chemisorption has been used for the characterization of the acid-base nature and coverage of the support materials by the active phase of a catalyst [22] and for the neutralization of basic sites in zeolites [23]. The CO₂ TPD conducted here show that the base strength of the zeolites decreases from NaX, NaA, Linde type 5A, NaOH treated Y, NaY to Na-ZSM-5, while the density of basic sites (under the influence of corona discharges) decreases from NaOH treated Y, NaX, Na-ZSM-5, NaY, NaA to Linde Type 5A, as shown in Table 1 (the amount of CO₂ adsorbed is referred to as the density of base sites). There is a significant plasma enhancement of zeolite basicities with NaOH treated Y, NaY and NaX. Both basicity and density of base sites were enhanced. However, a significant reduction in the base site density was observed with NaA and Linde type 5A. This could be the reason that somewhat lower PCMC activities were obtained with NaA and Linde type 5A. Na-ZSM-5 possesses neither acidic nor basic hydroxyls. No significant change is observed in the base sites of Na-ZSM-5. These results suggest that a significant plasma effect occurs on zeolites containing acidic or basic hydroxyls. This also supports a mechanism in which the role of OH groups is important for PCMC [8]. The order of base site density with zeolites under the influence of plasmas are almost in the same order of plasma catalytic activity from high to low, as reported previously [17]. Previous results [8] have suggested that the interaction between plasmas and catalysts induces a significant change both in the plasma and in the catalyst surface reactions. Secondary electron emissions are thought to be responsible for part of the unusual PCMC performance of zeolites. Two paths could lead to significant secondary electron emissions. Itoh *et al.* [24] have correlated the overall acid-base property of the zeolite with the arithmetic mean of the electrostatic potentials of the cations. Ward [20,21,25] also analyzed the variation of the hydroxyl content and Bronsted acidity of the various alkaline earth forms and considered [25] that the small cations with their associated high

Table 1. CO₂ adsorbed on zeolites (applied voltage: 6 kV; applied power: 7 w for plasma CO₂ chemisorption; the reactive conditions for methane conversion see ref.[17])

zeolite	CO ₂ chemisorption condition	gas temperature for CO ₂ chemisorption	amount of CO ₂ adsorbed (μmol/g)	plasma effect on CO ₂ adsorbed amount	CH ₄ ⁽¹⁸⁾ conversion at 50°C(%)	C ₂ ⁽¹⁸⁾ selectivity (%)
NaOH treated Y	no discharge	50°C	21.8		0.0	0.0
NaOH treated Y	with gas discharge	50°C	25.3	+16.1%	50.0	25.0
NaOH treated Y	no discharge	500°C	18.2		0.0	0.0
NaOH treated Y	with gas discharge	500°C	22.5	+23.7%	50.0	25.0
NaX	no discharge	50°C	18.4		0.0	0.0
NaX	with gas discharge	50°C	19.4	+5.4%	48.1	33.7
NaZSM-5	no discharge	50°C	17.2		0.0	0.0
NaZSM-5	with gas discharge	50°C	17.0	-1.1%	44.6	31.2
NaY	no discharge	50°C	12.4		0.0	0.0
NaY	with gas discharge	50°C	16.7	+34.3%	45.4	30.1
NaA	no discharge	50°C	16.6		0.0	0.0
NaA	with gas discharge	50°C	15.9	-4.2%	41.2	24.8
Linde type 5A	no discharge	50°C	11.2		0.0	0.0
Linde type 5A	with gas discharge	50°C	10.8	-3.6%	39.9	27.6

electrostatic field and polarizing power would result in the equilibrium moving towards dissociation, while larger cations would be expected to produce less dissociation. When the electrostatic potential is sufficiently high, an intense electric field will be formed within the zeolitic framework and electron emissions are induced.

The electron emissions from the zeolite appear to significantly enhance the PCMC reactions in the plasma phase, while the zeolite also provides a large surface area for heterogeneous reactions, either by the generation of radical cations, or by reactions occurring on polarized or non-polarized acidic or basic sites.

Different carbonaceous species have also been found to have been formed on different zeolites during PCMC. The carbonaceous deposits formed during PCMC over NaZSM-5 have a negative effect on PCMC and at the same time the stable streamer discharges shift to arc-like discharges. The active plasma region is thereby reduced significantly and PCMC activity is observed to decrease, as has been discussed previously [8,17]. The carbonaceous species formed on NaX, NaY, NaA or Linde type 5A are much less in amount and do not negatively affect the PCMC activity, compared to NaZSM-5. The

carbonaceous deposits on NaZSM-5 may act as electron scavengers and decrease its capability for electron emissions. TPO characterization has been conducted and the TPO spectra show more carbonaceous deposits formed on NaZSM-5 compared to the other two zeolites, NaX and NaOH treated Y zeolite. NaZSM-5 shows a specific TPO peak between 600K and 840K with a small low-temperature shoulder. The TPO spectrum for NaX does not contain this peak, while the spectrum for NaOH treated Y zeolite shows a small peak falling into this temperature scope. This large peak may be responsible for the shift of streamer discharges to the arc-like discharges and for the reduction in PCMC activity. Both NaX and NaOH treated Y zeolite show a wide smaller peak between 400K and 750K. These carbonaceous species evidently do not cause reduction in the PCMC activity during 4-hour PCMC experiments.

It was mentioned above that PCMC includes heterogeneous and homogeneous (plasma phase) reactions. The TPO experiments show that different carbonaceous species exist on the catalyst surface. These carbonaceous species may be involved in plasma reactions. Also, the plasma regeneration of used zeolites from PCMC, using 5% O₂ in helium with a total flowrate of 50 ml/min at 50 – 200°C, produced not only carbon dioxide, but also hydrogen, carbon monoxide, acetylene, ethylene and ethane. In order to better understand the reactions which occur on the catalyst surface under the influence of plasmas, a two-step PCMC over NaY was conducted to investigate plasma heterogeneous reactions of chemisorbed methane. The amount of chemisorbed methane over 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 catalytic reactions. Only methane was detected (without any detectable C₂ hydrocarbons) using a pure helium plasma, but essentially 100 percent methane conversion was achieved when other co-reactants were used. 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. It is shown that the hydrogen containing plasma induces the most selective production of C₂ hydrocarbons. CO₂ and O₂ containing plasmas also produce some C₂ products. This result suggests that active plasma species, like O[•], H, O(¹D) and so on, play an important role in the formation of higher hydrocarbons during the plasma heterogeneous methane conversion.

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 (°C)	selectivities (%)			
				C ₂ H ₆	C ₂ H ₄	CH ₄	CO
CO ₂ /He	1/39.2	20	250	5.1	2.2	84.0	8.7
O ₂ /He	1/49.0	20	150°	3.1	0.0	79.3	17.6
He	–	20	150	0.0	0.0	100.0	0.0
H ₂	–	20	150	10.0	4.1	85.9	0.0

4. CONCLUSIONS

The presence of certain zeolites with significant basicity, such as NaX and Y zeolites tested here, can stabilize sustained streamer corona discharges at low temperatures for methane conversion. The PCMC reactions form carbonaceous deposits on zeolites. The formation of such carbonaceous species depends upon the zeolite used. The carbonaceous deposits on NaZSM-5 have a negative influence on PCMC, while the “low temperature” coke formed on NaX and NaOH treated Y zeolite do not have a negative effect during a four hour reaction period. The basicity, polarity and thereby the reactivity of zeolites are modified by the plasma. This modification can be explained as a polarization effect on the electrostatic potential of zeolites and from the irradiation of the zeolite during plasma reactions. The OH groups in the zeolites significantly promote modification. The active species in the plasma phase are very helpful for the formation of higher hydrocarbons during plasma heterogeneous chemical processing, while a hydrogen containing plasma leads to the most selective production of higher hydrocarbons.

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REFERENCES

1. J. Huang, M.V. Badani, S.L. Suib, J.B. Harrison and M. Kablauoi, *J. Phys. Chem.*, 98(1994)206.
2. M.B. Kizling and S.G. J., *Appl. Catal. A*, 147(1996)1.
3. B. Eliasson, U. Kogelschatz, B. Xue and L.M. Zhou, Application of dielectric-barrier discharges to the decomposition and utilization of greenhouse gases, 13th International Symposium on Plasma Chemistry (ISPC-13), Beijing, August, 1997.
4. M. Venugopalan and S. Veprek S., in F.L. Boschke (Editor), *Topics in Current Chemistry*, Springer-Verlag, New York, 1993, p.3.
5. A. Marafee, C.-J. Liu, G.-H. Xu, R. Mallinson and L. Lobban, *Ind Eng. Chem. Res.*, 36(1997)632.
6. D.E. Rapakoulias, S. Cavadias and D. Mataras, *High Temp. Chem. Processes*, 2(1993)231.
7. J.A. Cairns, J.P. Coad, E.W.T. Richards and L.A. Stenhouse, *Nature*, 288(1980)686.
8. C.-J. Liu, A. Marafee A., B.J. Hill, R. Mallinson and L. Lobban, *Appl. Catal. A*, 164(1997)21.
9. S.L. Suib and R.P. Zerger, *J. of Catal.*, 139(1993)383.
10. V.F. Kiselev and O.V. Krylov, *Adsorption processes on semiconductor and dielectric surfaces I*, Springer-Verlag, New York, page 214(1985).
11. K. Jogan, A. Mizuno, T. Yamamoto and J.-S. Chang, *IEEE Trans. on Ind. Appl.*, 29(1993)876.
12. T. Yamamoto, K. Mizuno, I. Tamori, A. Ogata, M. Nifuku, M. Michalska and G. Prieto, *IEEE Trans. on Ind. Appl.*, 32(1996)100.
13. T. Yamamoto, K. Ramanathan, P.A. Lawless, D.S. Ensor, J.R. Newsome, N. Plaks and G.H. Ramsey, *IEEE Trans. on Ind. Appl.*, 28(1992)528.
14. R.-H. Zhang, T. Yamamoto and D.S. Bundy, *IEEE Trans. on Ind. Appl.*, 32(1996)113.
15. B. Eliasson and U. Kogelschatz, *IEEE Trans. on Plasma Sci.*, 19(1991)1063.
16. J.G. Birmingham and R.R. Moore, US Patent 4,954,320.
17. C.-J. Liu, R. Mallinson and L. Lobban, Under revision for *J. Catalysis*, June 1998.
18. L. Guzzi, K.V. Sarma and L. Borkó, *Catal. Lett.*, 39(1996)43.
19. W. Przystajko, R. Fiedorow and I.G. Dalla Lana, *Zeolites*, 7(1987)477.
20. J.W. Ward, *J. of Catal.*, 22(1971)237.
21. J.W. Ward, *J. of Catal.*, 14(1969)365.
22. F.M. Mulcahy, K.D. Kozminski, J.M. Slike, F. Ciccone, S.J. Scierka, M.A. Eberhardt, M. Houalla and D.M. Hercules, *J. of Catal.*, 139(1993)689.
23. C. Mirodatos, P. Pichat and D. Barthomeuf, *J. of Phys. Chem.*, 80(1996)1335.
24. H. Itoh, T. Hattori, K. Suzuki and Y. Murakami, *J. of Catal.*, 79(1983)21.
25. J.W. Ward, *J. of Catal.*, 10(1968)34.
26. C. Benndorf, P. Joeris and R. Krüger, *Pure & Appl. Chem.*, 66(1994)1195.
27. A. Grill, *Cold Plasma in Materials Fabrication: from Fundamentals to Applications*, IEEE Press, New York, 1994.
28. D.W. Werst, E.E. Tartakovsky, E.A. Picos and A.D. Trifunac, *J. Phys. Chem.*, 98(1994)10249.
29. D.W. Werst, E.A. Picos, E.E. Tartakovsky and A.D. Trifunac, *Chem. Phys. Lett.*, 229(1994)421.
30. D.W. Werst and P. Han, *Catal. Lett.*, 45(1997)253.
31. X.-S. Liu, G.-H. Zhang and J.K. Thomas, *J. Phys. Chem. B.*, 101(1997)2182.
32. X.-S. Liu, G.-H. Zhang and J.K. Thomas, *J. Phys. Chem. B.*, 99(1997)10024.
33. J.K. Thomas, *Chem. Rev.*, 93(1993)301.
34. C.-J. Liu, A. Marafee, B.J. Hill, G.-H. Xu, R. Mallinson and L. Lobban, *Ind. Eng. Chem. Res.*, 35(1996)3295.