[Review Paper]

Application of Nonthermal Plasma to Chemical Reactions

Shigeru FUTAMURA*, Hajime KABASHIMA, and Hisahiro EINAGA

National Institute of Advanced Industrial Science and Technology, AIST Tsukuba West, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, JAPAN

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Applicability of nonthermal plasma (NTP) to chemical reactions such as removal of hazardous air pollutants (HAPs), hydrogen production from small molecules, and hydrocarbon reforming is discussed on the basis of NTP-generating methods, the physicochemical nature of NTP, the reaction behavior of N_2 , O_2 , volatile organic compounds, and nitrogen oxides, and synergistic effects of NTP and catalysts/photocatalysts. Plasma-generating methods greatly affect the mean electron temperature and the distribution of active species formed in NTP. Hybridization of NTP with catalysts/photocatalysts is mandatory to increase the energy efficiency of the reaction system. Issues for practical application of NTP is discussed, using HAPs control as an example. The results of the authors' feasibility study indicate that the scale-up merit of the NTP reactor depends on the plasma-generating method.

Keywords

Nonthermal plasma, Air pollutants control, Hydrogen production, Reforming, Mechanism

1. Introduction

Nonthermal plasma (NTP), which is also called non-equilibrium plasma, is quite different from thermal plasmas such as those generated by plasma torches, arc discharge, and microwave discharge¹⁾. In NTP, only the motion of electrons is accelerated by an electric field and they capture high kinetic energies. Their temperature normally reaches 8000 to 80,000°C²⁾, but their lifetimes are shorter than 100 ns. Only high-energy electrons (e^*) are present in NTP because the electric field dies away before the motion of the molecules and ions is accelerated. NTP allows the design of unique reaction systems which cannot be realized in conventional chemical reaction media because the high energies of e^* are acquired by maintaining the gas at ambient temperature. Compared to e-beam processes where electron energies are higher than 100 kV³⁾, magnitudes of e^* energies are much smaller and no X-rays are generated in NTP. All of these characteristics combine to allow the construction of compact reactor systems for technologies based on NTP.

NTP has been applied to simultaneous removal of NO_x and SO_x ^{4),5)} and decomposition of poison gases since the 1980s. Recently, NTP has been extensively investigated to develop cost-effective systems for removal of ozone (O_3)-depleting substances^{6),7)}, volatile organic compounds (VOCs) causing an increase in tropo-

spheric O_3 ^{8)~10)}, and chemical substances causing global warming^{11)~13)}. NTP is also applicable to waste water control¹⁴⁾.

Syntheses of ammonia¹⁵⁾ and hydrazine¹⁶⁾ from N_2 and H_2 and methanol synthesis from methane¹⁷⁾ have been reported, but sufficiently high yields of the products have not been obtained. Quite recently, the potential of NTP has been investigated in the fields of oxidative coupling of methane^{18)~20)}, hydrogen production^{21)~23)}, and reforming of hydrocarbons^{20),24)~26)}.

Various methods are available to produce stable NTP at ambient temperature and atmospheric pressure, but the distributions of e^* energies and active oxygen species generated *in-situ* depend greatly on the method generating NTP^{21),23)}.

Research interest has been shifting to hybridization of NTP with adsorbents²⁷⁾ or catalysts^{21),26),28)~30)}. The major focus is on the synergistic interactions between NTP and catalysts. The hybridized reactor is the most promising cost-effective apparatus for Hazardous Air Pollutants (HAPs) control, and its practical applications have been extensively investigated worldwide.

This review describes the methods generating NTP, the elementary physicochemical nature of NTP, the reaction behavior of VOCs and nitrogen oxides, interactions between NTP and catalysts/photocatalysts, and the issues for practical application of NTP to chemical reactions.

* To whom correspondence should be addressed.

* E-mail: s-futamura@aist.go.jp

Fig. 1 Typical Nonthermal Plasma Reactors

2. Methods for NTP Generation

Typical discharge types used in VOC decomposition, etc. can be classified into barrier discharge, pulsed corona discharge (**Fig. 1 (3)**), and surface discharge (**Fig. 1 (4)**). Barrier discharge can be further divided into silent discharge (**Fig. 1 (1)**) and partial discharge generated in a reactor packed with ferroelectric materials (**Fig. 1 (2)**).

Silent discharge plasma reactors have been used as ozonizers. In these types of reactors, some dielectric materials are placed between the electrodes and voltages up to several kHz are applied to the reactor. The maximum gap distance for this type of reactor is 3-5 mm, and parallel alignments of the reactor modules are necessary in treating large quantities of gasses. Several types of electrode forms are utilized: plate-plate^{31,32}, wire-wire^{26,33}, wire-cylinder¹², and wire-plate.

Ferroelectric ceramic pellets such as BaTiO₃ are packed between the electrodes in packed-bed reactors. The dielectric constant of BaTiO₃ at room temperature should be higher than 3000, and almost no difference has been observed in plasma intensity for BaTiO₃ pellets with dielectric constants from 5000 to 15,000. Application of up to 10 kHz ac to the reactor polarizes each pellet, resulting in pulsed microdischarge in ns order between the contact points of the pellets. The reactors are usually parallel plate-plate cylinder (**Fig. 1 (2)**)³⁴ and coaxial cylinder types²³.

Wire-cylinder (**Fig. 1 (3)**)^{12,35} or wire-plate type electrodes are used for pulsed corona reactors, where voltage rise-time is as rapid as 10-50 ns, and application of very short pulsed voltages with half widths of 50-500 ns generates streamer coronas between the electrodes. Normally, positive pulsed discharge is used since higher plasma intensity is obtained. Rotary spark gaps³⁵ and thyatrons¹² are used as pulse generators. Impedance matching should be taken into

Table 1 Characteristic Parameters of Discharges

Parameter		Glow	Corona	Silent
Pressure	[MPa]	$< 10^{-3}$	0.1	0.1
Electric field	[kV/cm]	0.01	0.5-50	0.1-100
Reduced field	[Td]	50	2-200	1-500
Electron energy	[eV]	0.5-2.0	5, variable	1-10
Electron density	[cm ⁻³]	10^8 - 10^{11}	10^{13}	10^{14}
Degree of ionization		10^{-6} - 10^{-5}	small, variable	10^{-4}

account to increase the efficiency of the pulsed power transfer.

Pulsed streamer discharge is generated by applying 5-50 kHz high voltages to the string-formed electrodes on the upper and lower sides of dielectric ceramics in surface discharge reactors (**Fig. 1 (4)**)⁶. The temperature of the ceramics is locally increased during reactions in these types of reactors, and the contributions of thermal reactions cannot be neglected. Recently, hybridization of this type of reactor and a silent discharge reactor³⁶ has been investigated to increase the decomposition efficiencies of VOCs and NO_x.

At this stage, it is difficult to apply NTP to selective chemical reactions since the distribution of e* energy cannot be easily controlled³⁷. However, plasma-generating methods do affect electron temperature and the distribution of active oxygen species under aerobic conditions^{12,23}. The potential of NTP as a unique reaction medium is expected to increase in the future.

3. Physicochemical Nature of NTP

Table 1 summarizes the characteristic parameters of glow, corona, and silent discharges. The large magnitude of the e* energy obtained at atmospheric pressure is the major characteristics and the average e* energy varies in the range of 3-5 eV. Electron temperature and its energy distribution have been simulated³⁸, but this kind of approach can be applied only to a restricted number of systems. Thus, the performances of different types of reactors cannot be evaluated uniformly at this stage. Electron density is higher by 2 to 6 orders for corona and silent discharges than for glow discharge. The degree of ionization is generally low in NTP and approximately 10^{-4} for silent discharge.

4. Reaction Mechanisms

4.1. General Mechanism

The reactivities of volatile compounds are greatly affected by the background gas since quite different discharge properties are obtained in inert gases such as He and Ar, H₂, N₂-O₂ mixtures, and the system of methane coupling where its concentration is extremely high. Here, the reaction behavior of background gasses and volatile substrates in N₂-O₂ mixtures^{39,40} is

Fig. 2 Initial Pathways for High-energy Electrons in Nonthermal Plasma

mainly discussed.

In NTP, various reactions are initiated by e^* (Fig. 2): excitation (Eq. (1)), dissociation (Eq. (2)), attachment (Eq. (3)), dissociative attachment (Eq. (4)), ionization (Eq. (5)), and dissociative ionization (Eq. (6)). Based on the cross section, Eqs. (5) and (6) are least likely to occur in the normal range of e^* energy in NTP^{(41), (42)}.

Ethylene and trichloroethylene are much more reactive than the corresponding dihydro-derivatives such as ethane and 1,1,2-trichloroethane⁽⁹⁾, so the mechanism of homolysis of the labile chemical bonds is likely to proceed *via* the excited states of the above compounds. VOC decomposition may proceed *via* the electron transfer mechanism since the VOC decomposition efficiencies were correlated with the inverse of ionization potential⁽³⁴⁾. However, no products reflecting this mechanism were obtained. Our results with a packed-bed reactor (FPR)^{(7), (9), (43), (44)} show that trichloroethylene and tetrachloroethylene are much more reactive than benzene and paraffins in N_2 in the region of low specific energy density [SED (kJ/l) = Plug-in power (kW)/Gas flow rate (l/s)] (Fig. 3). Therefore, it is much less likely that VOC cation radicals are formed *via* the electron transfer mechanism.

The decomposition of trichloroethylene and tetrachloroethylene may involve Eq. (4) ($\text{A}^- = \text{Cl}^-$). The decomposition efficiencies of these polychlorohydrocarbons seem to depend on the number of chlorine atoms in them, but chloride ions do not accelerate their secondary decomposition. These observations suggest that homolytic cleavage of C-Cl bonds predominates over dissociative attachment and that chlorine atoms induce their secondary decomposition through addition and hydrogen atom abstraction. By-product analyses also support the radical mechanism⁽³⁵⁾. We have observed that the highest energy efficiency is obtained for a pulsed corona reactor in reaction systems where chemically induced decomposition by fragment radicals occurs as in trichloroethylene decomposition⁽¹²⁾. There is no difference in the energy efficiencies of silent discharge and packed-bed reactors. Since the

Reactor: FPR; background gas: dry air; initial VOC concentration: 1000 ppm.

Fig. 3 VOC Reactivities in Dry Air

lifetime of e^* is as short as 100 ns, this kind of chemically induced decomposition contributes to the increase in the energy efficiency of the reactor.

4. 2. Active Oxygen Species

As described in Section 3., the maximum energy of e^* in NTP reaches 10 eV, and endothermic bond cleavage occurs fairly easily for N_2 and O_2 . Nitriles are formed as by-products in VOC decomposition in N_2 ⁽⁴³⁾. However, only trace amounts of organic by-products are formed in air, and VOCs are oxidized to CO and CO_2 . We have found that 5% of oxygen content in N_2 - O_2 is adequate to oxidize organic intermediates to CO and CO_2 ⁽⁴⁴⁾. To complete the oxidative decomposition of VOCs, catalysts with high oxidation activities should be used because oxidation of CO to CO_2 is slow in NTP even in the presence of water⁽⁴⁴⁾.

The behavior of active oxygen species generated in NTP was investigated in a silent discharge plasma reactor⁽⁴⁵⁾. Triplet oxygen atoms ($\text{O}(^3\text{P})$) and singlet oxygen atoms ($\text{O}(^1\text{D})$) are formed in the initial reaction of O_2 and e^* . The maximum concentration is higher for $\text{O}(^3\text{P})$, and its lifetime is approximately 7 ms, whereas that of $\text{O}(^1\text{D})$ is shorter than 100 ns. O_3 is formed 10 ns after the discharge onset, but its maximum concentration is as only 1/100 high as that of $\text{O}(^3\text{P})$.

We have found that the plasma-generating method affects the O_3 formation behavior in NTP reactors⁽¹²⁾. Only 1-2 ppm of O_3 is generated from air in FPR, while 400-800 ppm of O_3 is formed in a silent discharge reactor (SDR) under the same conditions. Since the catalytic effect of BaTiO_3 on O_3 decomposition is negligible at ambient temperature⁽⁴⁶⁾, one interpretation is that O_3 decomposes inside the reactor due to locally high temperatures in microdischarge areas between the con-

tact points of the BaTiO₃ pellets. Gaseous oxygen accelerates trichloroethylene decomposition in SDR, but not in FPR¹². Since O(³P) is much more reactive with trichloroethylene than O₃⁴⁷, the key active oxygen species is considered to be O(³P).

The contribution of O(³P) may be much higher than that of OH radical in the oxidative decomposition of hydrocarbons in NTP based on the kinetic analysis of competitive oxidation reactions of acetylene and propylene in a silent discharge plasma reactor⁴⁸. Decreased decomposition rates for acetone, benzene, and ethylene were observed with increased reaction temperature from 25 to 300°C in a pulsed corona reactor⁴⁹. This trend well correlates with the temperature effect on the rate constants for the reactions of the above VOCs with O(³P).

O(¹D) is too short-lived to directly react with VOCs in NTP. OH radicals derived from the reaction of water and O(¹D) trigger the formation of various pollutants in the atmosphere⁵⁰. On the other hand, the rate-accelerating effect of OH radical has not been ascertained in any VOC decomposition reactions in NTP. In fact, water in the background gas tends to decrease decomposition efficiencies of VOCs at fixed SEDs, irrespective of their chemical structures¹².

5. Synergy between NTP and Catalysts

Even highly endothermic reactions can proceed more rapidly in NTP than in conventional chemical reaction media due to the large magnitudes of *e*^{*} energies. However, CO₂ cannot be obtained quantitatively because of the short lifetime of *e*^{*} and insufficient oxygen activation.

The possible synergistic effects anticipated between NTP and catalysts are as follows: (1) enhancement of *e*^{*} energy in NTP in the presence of catalysts, (2) promotion of bond cleavage resulting from the NTP-aided enhancement of intermolecular interactions between VOCs and catalysts, (3) activation of photocatalysts by NTP emission and promotion of VOC oxidation, and (4) control of active oxygen species by catalysts and increases in VOC decomposition efficiencies and CO₂ selectivities.

Regarding Item (1), it has been reported that electron temperature is elevated by impregnating precious metals on electrodes in a kind of silent discharge plasma reactor²¹. Item (2) is the essence of the interaction between NTP and catalysts, but almost no experimental evidence has been accumulated yet. Regarding Item (3), fundamental researches have been carried out with different reactor geometries. Since NTP emission wavelengths are adequate to excite TiO₂, a hybrid reactor comprising NTP and a photocatalyst can be developed. No independent light source is necessary, and the energy efficiency of the hybrid reactor can be

Reactor: SDR; initial benzene concentration: 106 ppm; MnO₂: 2 g; background gas: dry air.

Fig. 4 Synergistic Effect of Nonthermal Plasma and MnO₂ on Benzene Conversion

improved drastically. At this stage, no clear experimental evidence has been obtained showing that the TiO₂ in the reactor is excited by NTP emission. Although the performance of the NTP reactor hybridized with a honeycomb TiO₂ has been investigated³⁰, the evaluation of its utility should be deferred because the reactivities of only highly adsorbed compounds such as alkylamines and hydrogen sulfide have been tested.

It is relatively easy to verify the utility of the reactor system for Item (4). O₃, which is formed in large amounts in silent discharge reactors, does not react rapidly with many VOCs, and is highly toxic, but can be utilized as a precursor of O(³P) in the presence of a suitable catalyst. **Figure 4** shows the catalytic effect of MnO₂ on benzene conversion in air with SDR serially connected to a MnO₂ bed²⁹. In the absence of MnO₂, benzene conversion reaches only 30% at 1.7 kJ/L of SED. In contrast, benzene conversion jumps to 90% in the presence of MnO₂ at the same SED. These facts clearly show that the apparent energy efficiency of this reactor increases by three times just by incorporating MnO₂ in spite of the same energy transfer efficiency. Much more energy can be saved by improving the energy transfer efficiency of the reactor.

6. Applicability of NTP Systems to Specific Chemical Reactions

In the preceding sections, the general mechanism for NTP reactions and involvement of active species were discussed. In this section, applicability of NTP systems will be discussed, using the examples of NO_x removal, VOC removal, H₂ production from small molecules, and hydrocarbon reforming.

Reactor: FPR; $Q = 0.5\text{--}1.5$ l/min.

Fig. 5 Plasma Chemical Reactivities of N_2O , NO , and NO_2 in Dry N_2

6. 1. NO_x Removal

From a practical point of view, NTP has been applied to NO_x (nitric oxide (NO) and nitrogen dioxide (NO_2)) control^(4),5),51). However, we think that NTP technology cannot compete with SCR (Selective Catalytic Reduction) processes for NO_x control in stationary sources such as power plants. Thus, the discussion here is focused on the control of NO_x from moving sources. The oxygen content is normally lower than 1% for gasoline engine exhausts, but higher than 10% for diesel engine exhausts. NO_x and nitrous oxide (N_2O) are formed from background $\text{N}_2\text{--O}_2$, depending on oxygen content, reactor type, and SED^(52)~57). NO_x can be directly decomposed to N_2 despite partial N_2O formation from NO_2 in systems where O_2 content is lower than 5%^(54),58).

Figure 5 shows the reactivities of N_2O , NO , and NO_2 in dry N_2 with FPR. Both NO and NO_2 can be decomposed in the lower SED range⁽⁵⁴⁾. On the other hand, N_2O decomposition cannot be achieved even at higher SEDs. However, NTP reactors operate as NO_x producers rather than as NO_x decomposers. Figure 6 shows that a threshold of oxygen content is present for NO_x formation from $\text{N}_2\text{--O}_2$ mixture gasses with FPR. The molar ratio of NO to NO_2 also depends on the oxygen content (Fig. 7). Figures 6 and 7 show that NO_x formation from $\text{N}_2\text{--O}_2$ in NTP is negligible at the oxygen content $\leq 5\%$ v/v and that NO_2 formation predominates over that of NO , irrespective of the oxygen content⁽⁵⁴⁾. In the presence of O_2 , NO and NO_2 are partially converted to each other in NTP.

The data in Figs. 5 to 7 suggest that NO_x in gasoline engine exhausts can be decomposed to N_2 only with NTP. On the other hand, NTP does not work for NO_x removal for diesel engine exhausts. The most promising approach could be oxidation of NO to NO_2 with

Reactor: FPR; $Q = 0.5\text{--}1.5$ l/min.

Fig. 6 Effect of O_2 Concentration on NO_x Formation from $\text{N}_2\text{--O}_2$ Mixture Gasses

Reactor: FPR; $Q = 0.5\text{--}1.5$ l/min.

Fig. 7 Effect of O_2 Concentration on the Composition of NO_x from $\text{N}_2\text{--O}_2$ Mixture Gasses

NTP, followed by catalytic reduction of NO_2 to N_2 , since the first step is energetically more favorable with NTP than with other approaches⁽⁵⁷⁾, but NO_2 cannot be completely reduced to N_2 with NTP in oxygen-rich gasses. The wet discharge plasma reactor⁽⁵⁷⁾ and the NTP-chemical process using Na_2SO_3 ⁽⁵¹⁾ as NO_2 absorber have been developed, but these methods cannot be recommended because of the need for secondary treatments of waste water and Na_2SO_4 .

6. 2. VOC Removal

Many aspects relevant to VOC control were discussed in Sections 3. and 4. Here, the reaction-controlling factors governing VOC removal are discussed.

Reactor FPR; hydrocarbon concentration 500 ppm; $Q = 0.5-1.5$ l/min.

(a) Benzene, (b) toluene, (c) cyclohexene.

Fig. 8 Background Effect on Hydrocarbon Conversions

Figure 8 shows the effects of background gas and SED on the conversions of benzene, toluene, and cyclohexene⁵⁹. Under dry conditions, cyclohexene is the most reactive, and toluene and benzene have shown almost the same reactivities. The reaction behavior of these hydrocarbons sharply contrasts with those in autoxidation and photooxidation systems. The data in Fig. 8 could not be stratified by gas flow rate. Since e^* disappears within 100 ns, there is no influence of

Reactor FPR; cyclohexene concentration 500 ppm.

(a) In dry N₂, $Q = 1.5$ l/min, applied voltage 7.0 kV.

(b) In wet N₂, $Q = 1.0$ l/min, applied voltage 6.9 kV.

Fig. 9 Gas Chromatograms Obtained from Reactions of Cyclohexene

residence time on the hydrocarbon conversion. Slightly higher conversions are obtained in dry air than in dry N₂ in the reaction of cyclohexene, but O₂ does not accelerate the decomposition of benzene or toluene. All these findings suggest that the rate-determining step is the energy transfer from e^* to the above hydrocarbons followed by the cleavage of the carbon-carbon bonds in the benzene rings. The contribution of the oxidative decomposition by some oxygen species is expected to be much smaller.

In the presence of water, almost the same or slightly lower conversions are obtained for the above three hydrocarbons. The additive effect of water is complicated in nonthermal plasma. As discussed in subsection 4.2., O(¹D) derived from O₂ can generate hydroxyl radicals in the reaction with H₂O. However, there has been no report on the acceleration of VOC decomposition rates by water. It is considered that H₂O quenches e^* rather than produces $\cdot$ OH, resulting in lower conversions of the hydrocarbons. The additive effect of water (Fig. 8) has been also observed in the decomposition of halogenated VOCs such as trichloroethylene³⁵, tetrachloroethylene⁹, and bromomethane⁷.

Figure 9 shows the gas chromatograms for the reaction mixtures obtained in the reactions of cyclohexene in dry N₂ (a) and in wet N₂ (b). Cyclohexene conversions are 56% for both of the reactions. In dry N₂,

Reactor FPR; benzene concentration 500 ppm, $Q = 0.5-1.5$ l/min.

Fig. 10 Carbon Balances Obtained from Benzene Decomposition

C-C bond cleavage predominates and hydrogen migration between cyclohexene molecules also occurs. Nitrogen is incorporated as cyano groups into inorganic and organic by-products. Quite a different by-product distribution is obtained in the presence of water. Nitrile formation is suppressed and oxygenation products are obtained. Cyclohexene oxide is not derived from the reaction of cyclohexene and $\cdot\text{OH}$, and this strongly active oxidant easily decomposes the epoxide structure. Since cyclohexanone is produced in the isomerization of cyclohexene oxide in NTP, the most plausible active oxygen species is $\text{O}(^3\text{P})$.

Under anaerobic conditions, only poor carbon balances are obtained in VOC decomposition, but almost all carbon atoms in reacted VOCs are recovered as CO_x ($x = 1$ and 2), irrespective of the water content in the reactant gas. **Figure 10** shows an example of benzene decomposition. **Figure 11** shows the CO_2 mole fraction as a function of benzene conversion. With an increase in benzene conversion, CO_2 selectivity slightly decreases in the presence or absence of water. The CO_2 mole fraction increase caused by increased water content can be ascribed to the water-gas-shift reaction promoted in NTP since the oxidation of CO to CO_2 is promoted to the same degree (**Fig. 12**)⁴⁴.

The most important point here is the operations of NTP reactors at low SEDs. Even in the presence of O_2 , which is necessary to oxidize organic intermediates, formation of undesirable nitrogen oxides can be suppressed. However, CO_2 selectivity is not high enough only with NTP. To promote the complete oxidation of VOCs and to increase the energy efficiency, use of catalysts/photocatalysts is mandatory as discussed in Section 5.

Reactor FPR; benzene concentration 500 ppm, $Q = 1.0$ l/min.

Fig. 11 Effect of Water on CO_2 Mole Fraction in Benzene Decomposition

Reactor FPR; CO concentration 1000 ppm, $Q = 0.5-1.5$ l/min.

Fig. 12 Background Effect on the Oxidation of CO to CO_2

6.3. Hydrogen Gas Production from Small Molecules

Hydrogen production from small molecules such as water^{21,23}, methanol²² and methane⁶⁰ has been reported with dielectric barrier discharge reactors as one of the extensions of NTP technology. NTP affords a unique methodology to continuously produce H_2 in the absence of any catalysts, compared to photocatalysis⁶¹ and mechano-catalysis⁶².

In the decomposition of halogenated VOCs such as trichloroethylene, bromomethane, and tetrafluoromethane, FPR and SDR have shown the comparable performances (**Fig. 13**)¹². These results are reasonable if almost the same magnitudes of plasma energy are consumed under the same SED conditions. On the other hand, FPR produced much more H_2 than SDR

Substrate concentration 1000 ppm, $Q = 0.5\text{--}1.5$ l/min.
(a) FPR, (b) SDR.

Fig. 13 Reactivities of Trichloroethylene, CH₃Br, and CF₄ in Dry N₂

from H₂O, CH₄, and CH₃OH (**Fig. 14**)⁶⁰. Here, H₂ yield is defined as $\text{H}_2 \text{ yield (mol\%)} = 100 \times [\text{H}_2 \text{ concentration (ppm)}] / [\text{Maximum concentration of H}_2 \text{ liberated from a feed substrate (ppm)}]$. The yield of H₂ is double from CH₄ and CH₃OH than from H₂O even if the same H₂ yields are obtained for these three compounds. Therefore, substrate reactivity decreases in the order: CH₃OH > CH₄ > H₂O. **Table 2** summarizes the ratios of H₂ yields from CH₄ and H₂O to those from CH₃OH at 5.0 kJ/l of SED. In nitrogen, almost the same ratios are obtained for CH₄/CH₃OH with either FPR and SDR. These findings reflect the different reactivities of these two compounds in specific NTP media. The parametric data in **Table 2** suggest that similar kinds of NTP are achieved in FPR and in SDR. Therefore, the large discrepancy in H₂ yields in **Fig. 14** indicates that higher electron temperature is obtained in FPR than in SDR since H₂ formation from these small molecules is more endothermic than the

Substrate concentration 1.0%, $Q = 100$ ml/min.
(a) FPR, (b) SDR.

Fig. 14 Reactivities of H₂O, CH₄, and CH₃OH in N₂

Table 2 Reactor Effect on Relative H₂ Yield

	H ₂ O/CH ₃ OH	CH ₄ /CH ₃ OH
FPR	0.17	0.32
SDR	0.12	0.33

Initial concentration of substrate 1.0%, $Q = 100$ ml/min.
SED was fixed at 5.0 kJ/l.

decomposition of the halogenated VOCs, which is partly promoted by reactive intermediates derived from the initial bond cleavage in the VOCs. Comparison of the reference data indicates that higher electron temperature is obtained in partial discharge with BaTiO₃ than in silent discharge^{21)–23),60}. Such pioneering research may elucidate the physicochemical natures of NTP reaction media formed in different types of reactors.

Irrespective of H₂ sources, an interesting trend has been observed that higher H₂ yield is obtained at shorter residence times²³. **Figure 15** shows an example of H₂O decomposition¹². Since H₂ is produced succes-

Reactor FPR, H₂O concentration 1.0%, $Q = 100$ ml/min.

Fig. 15 Effect of Gas Flow Rate on H₂ Yield in Water Decomposition in N₂

Reactor FPR, water concentration 1.0%, $Q = 100$ ml/min, applied voltage 7.6-8.0 kV.

Fig. 16 Time Profile of H₂ Yield during the Continuous Decomposition of Water

sively from the small molecules in NTP, these substrates are considered to be regenerated from their reaction intermediates and hydrogen atoms.

Table 3 summarizes the major products obtained in the reactions of H₂O, CH₄, and CH₃OH. In the reaction of H₂O, no products were detected by GC-MS other than H₂ and O₂. In the reactions of CH₄ and CH₃OH, CO formation predominated over that of CO₂ and light hydrocarbons were also formed as by-products. In the reaction of CH₄, the oxygen source can be ascribed to BaTiO₃. No O₂ was formed from CH₃OH. The higher CO_x yield and the higher selectivity for CO₂ in this reaction suggest the involvement of the CH₃OH oxygen atom in the oxidation of carbon radicals and CO to CO₂.

Figure 16 shows that H₂ can be produced for 10 h. These data suggest that stable microdischarge can be maintained between the contact points of BaTiO₃ if *ca.* 1% v/v of H₂O is continuously fed to FPR.

Hydrogen production from different sources have been extensively investigated with NTP and thermal plasma because of the future potential as a clean energy source for fuel cell vehicles, public facilities, and households. NTP equipments can start instantly only by electricity, and this characteristic will extend its applicability to different fields for H₂ utilization.

6. 4. Hydrocarbon Reforming

Steam reforming of methane is the best method to produce H₂ by minimizing the amount of CO₂, compared to CO₂ reforming and partial oxidation of heavier paraffins and coal⁶³. Among the hydrocarbons, methane is the most abundant and hydrogen-rich gas. There are three main reaction modes for methane reforming: steam reforming, partial oxidation, and carbon dioxide reforming. The above processes give different synthesis gas compositions⁶⁴. In NTP, partial oxidation processes are not favorable because expensive H₂ is consumed in the reaction with O₂ to form water. The other two processes are attractive reactions to be carried out in NTP. Steam reforming is a highly endothermic reaction, and the high energies of e^* can be utilized to the full potential. In NTP media, CO₂ can act as an oxidant, and the reaction product CO is stable⁴⁴. In catalytic CO₂ reforming processes, carbon deposition is not neglected, and catalyst deactivation often interrupts the development of commercialized processes.

Hitherto, dielectric barrier discharge reactors have been applied to these reactions, and the effects of reactor type²⁰, feed gas composition^{25,26}, gas pressure²⁵,

Table 3 Major Products Obtained from the Decomposition of Water, Methane, and Methanol with FPR

Substrate	Conversion [mol%]	Products [ppm]
H ₂ O		H ₂ (1866), O ₂ (252)
CH ₄	32	H ₂ (4847), C ₂ HCs ^{a)} (84), CO (413), CO ₂ (21)
CH ₃ OH	76	H ₂ (11790), C ₂ HCs ^{a)} (114), CH ₄ (1407), CO (4040), CO ₂ (1238)

Reactor FPR, initial substrate concentration 1.0%, $Q = 100$ ml/min, plug-in power 20 W.

a) C₂ HCs denotes the hydrocarbons such as ethane, ethylene, and acetylene. Values in parentheses denote the total concentrations of these hydrocarbons with 2 carbon atoms.

Reactor FPR, paraffin concentration 1.0%, H₂O 2.0%, $Q = 100$ ml/min.

Fig. 17 Reactivities of Selected Paraffins in Steam Reforming in N₂

SED²⁵⁾, and reaction temperature²⁵⁾ have been investigated. As described in subsection 4.2., synergistic effects of NTP and catalysts are of much interest in this field²⁶⁾.

We have been exploring the potential of NTP in the processes of hydrocarbon reforming, focusing on its applicability to different types of hydrocarbons and factors governing hydrocarbon conversion, CO_x ($x = 1$ and 2) selectivity, and [H₂]/[CO].

In the steam reforming of methane, ethane, propane, and neopentane [CH₃C(CH₃)₂CH₃] in N₂ with FPR, conversions are almost the same for the latter three hydrocarbons and higher than for CH₄ (Fig. 17)⁶⁵⁾. These findings do not reflect the different liabilities of the carbon-carbon bonds in the substrate hydrocarbons, and alkyl radicals are less likely to induce their secondary decomposition.

Table 4 summarizes the conversions of the four hydrocarbons under fixed experimental conditions and the distributions of the major products. Formation of gaseous oxygen was not observed in any of these reactions. In the reaction of methane, H₂ was the major product, and formation of C₂ hydrocarbons such as ethane, ethylene, and acetylene was negligible com-

pared to that of CO and CO₂. Oxidative coupling of methyl radicals is less likely to occur, compared to their oxidation to CO and CO₂. In the reactions of ethane, propane, and neopentane, the concentration ratio of H₂ to CH₄ decreased with larger carbon number of the hydrocarbon in spite of higher concentrations of H₂. These findings suggest that even in NTP, methane is the substrate giving the highest H₂ yield among the hydrocarbons.

In these reactions, oxygen atoms mainly come from water, and its initial content is the same for all of the hydrocarbons. However, the concentrations of CO and CO₂ highly depend on the numbers of carbon and hydrogen atoms present in the substrate hydrocarbon. The CO₂ concentration decreases with larger carbon number of the hydrocarbon. These findings suggest that the rate for CO₂ formation is controlled by the supply of oxygen atoms from water. Furthermore, the actual amount of H₂ formed is larger for the hydrocarbons with more hydrogen atoms per molecule. These findings indicate that CO₂ is reduced by H₂ in the reaction systems of ethane, propane, and neopentane.

Figure 18 shows that the H₂ yield is the highest for CH₄, and lower H₂ yields are obtained for the other hydrocarbons. These data indicate that the largest number of hydrogen atoms per molecule does not give the highest efficiency for H₂ formation in NTP media,

Reactor FPR, paraffin concentration 1.0%, H₂O 2.0%, $Q = 100$ ml/min.

Fig. 18 H₂ Yields in the Steam Reforming of Selected Paraffins in N₂

Table 4 Major Products Obtained from the Steam Reforming of Hydrocarbons with FPR

Substrate	Conversion [mol%]	Products [ppm]
CH ₄	29	H ₂ (7242), C ₂ H ₆ (7), C ₂ H ₄ (3), C ₂ H ₂ (2), CO (1486), CO ₂ (1410)
CH ₃ CH ₃	52	H ₂ (9834), CH ₄ (1479), C ₂ H ₄ (164), C ₂ H ₂ (101), CO (2471), CO ₂ (806)
CH ₃ CH ₂ CH ₃	52	H ₂ (10894), CH ₄ (2441), C ₂ H ₆ (315), C ₂ H ₄ (302), C ₂ H ₂ (158), CO (2433), CO ₂ (584)
CH ₃ C(CH ₃) ₂ CH ₃	53	H ₂ (13004), CH ₄ (4010), C ₂ H ₆ (292), C ₂ H ₄ (400), C ₂ H ₂ (184), CO (2398), CO ₂ (487)

Initial concentrations of substrate hydrocarbons and water were 1.0% and 2.0%, respectively.
 $Q = 100$ ml/min, plug-in power 20 W.

Reactor FPR, paraffin concentration 1.0%, H₂O 2.0%, $Q = 100$ ml/min.

Fig. 19 Molar Ratio of H₂ to CO in Steam Reforming of Paraffins in N₂

Fig. 20 Plausible Mechanism for Steam Reforming of Paraffins with Nonthermal Plasma

although the actual H₂ amount from neopentane almost doubles that from methane.

In our experiments without catalysts, [H₂]/[CO] exceeded 3.5 for the reactions of all the hydrocarbons (Fig. 19). These data are comparable to those for the processes of methane steam reforming with catalysts at elevated temperatures⁶⁴. For ethane and propane, [H₂]/[CO] was almost constant. A maximum was observed for methane, and [H₂]/[CO] increased with SED for neopentane. In the reaction of methane, CO₂

selectivity was higher than for the other hydrocarbons (Table 4). This means that H₂ was not consumed in CO₂ reduction (Fig. 20), and CO concentrations could be kept low. Therefore, higher ratios can be obtained for methane.

7. Practical Application of NTP

One of the authors (S. F.) attended 15th International Symposium on Plasma Chemistry held in Orléans, France in July, 2001. In one of the sessions, Professor A. Fridman of Chicago University started the discussion with the floor on the issues of NTP technology for practical application to HAPs control. All participants agreed on the significance of the following three items: (1) development of cost-effective systems for HAPs control, (2) suppression of hazardous by-products, and (3) development of power supplies with high power. On the basis of the treatment of NO_x-SO_x, power consumption should be lowered to 10 Wh Nm⁻³. This value is the smallest obtained independently by one of the authors on the basis of the reference data⁶⁶ (Table 5). Further cost reduction is mandatory, but can be achieved by increasing the energy efficiencies of NTP reactors hybridized with catalysts/photocatalysts (Section 5.) and by reducing gas amounts with conventional VOC condensers such as honeycomb rotors. Under conditions promoting oxidative decomposition of HAPs, the levels of organic intermediates and CO are considered to be lower than their emission standards. In the silent discharge plasma-MnO₂ reactor (Section 5.), 93% benzene conversion and 90% CO₂ selectivity are obtained in air in the presence of water²⁹. As described in Subsection 6.2., formation of nitrogen oxides cannot be neglected, depending on the operating conditions of the NTP reactors⁵⁴. In this context, low-power operation of NTP reactors should be significant. From the practical point of view, high power supplies are necessary. However, operating conditions should be carefully selected to keep the run-

Table 5 Comparison of Reactor Power Consumption for Nonthermal Plasma Technology

	Pulsed corona [Wh Nm ⁻³]	Silent corona [Wh Nm ⁻³]	Packed bed [Wh Nm ⁻³]	Surface discharge [Wh Nm ⁻³]
Bench-scale	24-100 ^{a)}	60-1000 ^{d)}	24-120 ^{g)}	30-150
Pilot-scale	4-16 ^{b)}	10-500 ^{e)}	10-30 ^{h)}	10-60 ^{h)}
Large-scale	2-6 ^{c)}	— ^{f)}	— ^{f)}	— ^{f)}

Note: conversion factor 1 Wh Nm⁻³ = 3.6 J l⁻¹.

a) Based on bench-scale unit (0.1 Nm³ h⁻¹).

b) Based on Masuda's 100 kV and 15 kV power supply (50 Nm³ h⁻¹).

c) Estimate based on Masuda's 200 kV power supply.

d) Based on bench-scale unit.

e) Based on Savannah River pilot-scale unit (5-9 Nm³ h⁻¹).

f) May not be suitable for large-scale unit.

g) Based on bench-scale unit (0.1 Nm³ h⁻¹).

h) Estimate based on bench-scale unit (reactor design modified).

ning cost low.

8. Concluding Remarks

This review described the background of NTP research aimed at HAPs control, NTP-generating methods, physicochemical nature of NTP, general mechanisms for NTP reactions, hybridization of NTP with catalysts/photocatalysts, NTP application to NO_x removal, VOC removal, H₂ production from small molecules, and hydrocarbon reforming, and future issues of NTP technology. NTP is one of the technologies under further development. Promotion of fundamental and applied researches is necessary because this technique has economical and environmental benefits if applied to specific purposes.

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References

- 1) Tanimoto, M., "Plasma," Denki-shoin, Tokyo (1990).
- 2) Beuthe, T. G., Chang, J. S., "Handbook of Electrostatic Processes," eds. by Chang, J. S., Kelly, A. J., Crowley, J. M., Marcel Dekker, (1995), p. 147.
- 3) Tokunaga, O., *J. Inst. Electrostatics Jpn.*, **19**, 296 (1995).
- 4) Clements, J. S., Mizuno, A., Finney, W. C., Davis, R. H., *IEEE Trans. Ind. Applicat.*, **25**, 62 (1989).
- 5) Higashi, M., Uchida, S., Suzuki, N., Fujii, K., *IEEE Trans. Plasma Sci.*, **20**, 1 (1992).
- 6) Oda, T., Takahashi, T., Nakano, H., Masuda, S., *IEEE Trans. Ind. Applicat.*, **29**, 787 (1993).
- 7) Zhang, A., Futamura, S., Yamamoto, T., *J. Air & Waste Manage. Assoc.*, **49**, 1442 (1999).
- 8) Yamamoto, T., Ramanathan, K., Lawless, P. A., Ensor, D. S., Newsome, J. R., Ramsey, G. H., Plaks, N., *IEEE Trans. Ind. Applicat.*, **28**, 528 (1992).
- 9) Futamura, S., Zhang, A., Yamamoto, T., *J. Electrostatics*, **42**, 51 (1997).
- 10) Evans, D., Rosocha, L. A., Anderson, G. K., Coogan, J. J., Kushner, M. J., *J. Appl. Phys.*, **74**, 5378 (1993).
- 11) Futamura, S., Einaga, H., Kabashima, H., Ibusuki, T., Proc., 3rd Int. Symp. on Non-Thermal Plasma Technology for Pollution Control, Jeju, Korea, 2001, p. 84.
- 12) Futamura, S., Einaga, H., Zhang, A., *IEEE Trans. Ind. Applicat.*, **37**, 975 (2001).
- 13) Urashima, K., Kostov, K. G., Chang, J.-S., Okayasu, Y., Iwaizumi, T., Yoshimura, K., Kato, T., *IEEE Trans. Ind. Applicat.*, **37**, 1456 (2001).
- 14) Sun, B., Sato, M., Clements, J. S., *J. Phys. D: Appl. Phys.*, **32**, 908 (1999).
- 15) Veprek, S., Venugopalan, M., (eds.), "Topics in Current Chemistry 107 Plasma Chemistry IV," Springer-Verlag, Berlin (1983), p. 4.
- 16) Tanaka, S., Uyama, H., Matsumoto, O., *Plasma Chem. Plasma Process.*, **14**, 491 (1994).
- 17) Yao, S., Takemoto, T., Ouyang, F., Nakayama, A., Suzuki, E., Mizuno, A., Okumoto, M., *Energy & Fuels*, **14**, 459 (2000).
- 18) Liu, C. G., Marafee, A., Hill, B. J., Xu, G. H., Mallinson, R., Lobban, L., *Ind. Eng. Chem. Res.*, **35**, 3295 (1996).
- 19) Liu, C. G., Mallinson, R., Lobban, L., *J. Catal.*, **179**, 326 (1998).
- 20) Yao, S. L., Okumoto, M., Nakayama, A., Suzuki, E., *Energy & Fuels*, **15**, 1295 (2001).
- 21) Chen, X., Marquez, M., Rozak, J., Marun, C., Luo, J., Suib, S. L., Hayashi, Y., Matsumoto, H., *J. Catal.*, **178**, 372 (1998).
- 22) Tanabe, S., Matsuguma, H., Okitsu, K., Matsumoto, H., *Chem. Lett.*, **2000**, 1116.
- 23) Kabashima, H., Einaga, H., Futamura, S., *Chem. Lett.*, **2001**, 1314.
- 24) Wang, S., Lu, G. Q., Millar, G. J., *Energy & Fuels*, **10**, 896 (1996).
- 25) Zhou, L. M., Xue, B., Kogelschatz, U., Eliasson, B., *Energy & Fuels*, **12**, 1191 (1998).
- 26) Kado, S., Urasaki, K., Sekine, Y., Fujimoto, K., *J. Chem. Soc., Chem. Commun.*, **2001**, 415.
- 27) Ogata, A., Ito, D., Mizuno, K., Kushiya, S., Yamamoto, T., *IEEE Trans. Ind. Applicat.*, **37**, 959 (2001).
- 28) Ogata, A., Yamanouchi, K., Mizuno, K., Kushiya, S., Yamamoto, T., *IEEE Trans. Ind. Applicat.*, **35**, 1289 (1999).
- 29) Einaga, H., Ibusuki, T., Futamura, S., *IEEE Trans. Ind. Applicat.*, **37**, 1476 (2001).
- 30) Son, G. S., Yun, S. W., Kim, D. J., Ko, S. H., Song, J. W., Lee, K. Y., Proc., 3rd Int. Symp. on Non-Thermal Plasma Technology for Pollution Control, Jeju, Korea, 2001, p. 250.
- 31) Brock, S. L., Marquez, M., Suib, S. L., Hayashi, Y., Matsumoto, H., *J. Catal.*, **180**, 225 (1998).
- 32) Brock, S. L., Shimojo, T., Marquez, M., Marun, C., Suib, S. L., Matsumoto, H., Hayashi, Y., *J. Catal.*, **184**, 123 (1999).
- 33) Kado, S., Sekine, Y., Fujimoto, K., *J. Chem. Soc., Chem. Commun.*, **1999**, 2485.
- 34) Nunez, C. M., Ramsey, G. H., Ponder, W. H., Abbott, J. H., Hamel, L. E., Kariher, P. H., *Air & Waste*, **43**, 242 (1993).
- 35) Futamura, S., Yamamoto, T., *IEEE Trans. Ind. Applicat.*, **33**, 447 (1997).
- 36) Chang, J. S., Urashima, K., Ito, T., "Emerging Technologies in Hazardous Waste Management VI," ed. by Tedder, D. W., ACS Press, Atlanta (1994), p. 203.
- 37) Yamamoto, T., *J. Inst. Electrostatics Jpn.*, **19**, 301 (1995).
- 38) Morgan, W. L., Penetrante, B. M., *Comp. Phys. Commun.*, **58**, 127 (1990).
- 39) Eliasson, B., *IEEE Trans. Plasma Sci.*, **19**, 1063 (1991).
- 40) Futamura, S., *J. Inst. Electrostatics Jpn.*, **21**, 9 (1997).
- 41) Becker, K. H., "Low Temperature Plasma Physics," eds. by Hippler, R., Pfau, S., Schmidt, M., Schoenbach, K. H., WILEY-VCH, Berlin (2001), p. 55.
- 42) Chang, M. B., personal communication.
- 43) Futamura, S., Zhang, A., Prieto, G., Yamamoto, T., *IEEE Trans. Ind. Applicat.*, **34**, 967 (1998).
- 44) Futamura, S., Zhang, A., Yamamoto, T., *IEEE Trans. Ind. Applicat.*, **35**, 760 (1999).
- 45) Eliasson, B., Kogelschatz, U., *J. Chim. Phys.*, **83**, 279 (1986).
- 46) Futamura, S., Zhang, A., Einaga, H., Kabashima, H., *Catal. Today*, **72**, 259 (2002).
- 47) Chang, W.-D., Senkan, S. M., *Environ. Sci. Technol.*, **23**, 442 (1989).
- 48) Hoard, J., Wallington, T. J., Bretz, R. L., Malkin, A., Proc., 3rd Int. Symp. on Non-Thermal Plasma Technology for Pollution Control, Jeju, Korea, 2001, p. 176.
- 49) Hsiao, M. C., Penetrante, B. M., Merritt, B. T., Vogtlin, G. E., Wallman, P. H., *J. Adv. Oxid. Technol.*, **2**, 306 (1997).
- 50) Wayne, R. P., "Chemistry of Atmospheres," 3rd ed., Oxford University Press, New York (2000).
- 51) Yamamoto, T., Yang, C.-L., Beltran, M. R., Kravets, Z., *IEEE Trans. Ind. Applicat.*, **36**, 923 (2000).
- 52) Hill, R. D., Rahmim, I., Rinker, R. G., *Ind. Eng. Chem. Res.*, **27**, 1264 (1988).

- 53) Penetrante, B. M., Hsiao, M. C., Merritt, B. T., Vogtlin, G. E., Wallman, P. H., *IEEE Trans. Plasma Sci.*, **23**, 679 (1995).
- 54) Futamura, S., Zhang, A., Yamamoto, T., *IEEE Trans. Ind. Applicat.*, **36**, 1507 (2000).
- 55) Ohkubo, T., Kanazawa, S., Nomoto, Y., Chang, J. S., Adachi, T., *IEEE Trans. Ind. Applicat.*, **30**, 856 (1994).
- 56) Mizuno, A., Shimizu, K., Chakrabarti, A., Dascalescu, L., Furuta, S., *IEEE Trans. Ind. Applicat.*, **31**, 957 (1995).
- 57) Mizuno, A., Shimizu, K., Matsuoka, T., Furuta, S., *IEEE Trans. Ind. Applicat.*, **31**, 1463 (1995).
- 58) Mätzing, H., *Adv. Chem. Phys.*, **80**, 315 (1991).
- 59) Futamura, S., Zhang, A., Einaga, H., Proc. The Asia-Pacific Workshop on Water and Air Treatment by Advanced Oxidation Technologies: Innovative and Commercial Applications, 1998, p. 87.
- 60) Kabashima, H., Einaga, H., Futamura, S., Conf. Rec., 36th IEEE-IAS Annual Meeting, 2001, p. 680; submitted for publication in *IEEE Trans. Ind. Applicat.*
- 61) Takata, T., Tanaka, A., Hara, M., Kondo, J. N., Domen, K., *Catal. Today*, **44**, 17 (1998).
- 62) Ohta, T., *Appl. Energy*, **67**, 181 (2000).
- 63) Armor, J. N., *Appl. Catal. A: General*, **176**, 159 (1999).
- 64) Pusakas, I., *CHEMTECH*, **1995**, 43.
- 65) Kabashima, H., Einaga, H., Futamura, S., Prep. 81st Annual Meeting of the Chemical Society of Japan, 2002, 2E6-29.
- 66) Yamamoto, T., Futamura, S., *Combust. Sci. Tech.*, **133**, 117 (1998).

要 旨

化学反応に対する低温プラズマの応用

二タ村 森, 梶島 一, 永長 久寛

産業技術総合研究所, 305-8569 茨城県つくば市小野川 16-1 産総研つくば西

低温プラズマの発生法と物理化学的な性質, 低温プラズマ中における窒素分子, 酸素分子, 揮発性有機化合物, 窒素酸化物の反応挙動, 低温プラズマと触媒/光触媒との相乗作用に関する知見を基にして, 有害大気汚染物質 (HAPs) の分解反応, 小分子からの水素生成, 炭化水素の改質といった化学反応に対する低温プラズマの応用可能性について論じた。低温プラズマの平均電子温度や生成する活性種の分布はプラズマ発生法に大

きく依存する。上記反応系のエネルギー効率を高めるために, 低温プラズマと触媒/光触媒との複合化は必須であろう。低温プラズマ技術実用化のための課題について HAPs 分解処理を例にして論じた。著者らの実験結果と文献データの比較により, 低温プラズマ反応装置のスケールアップはプラズマ発生法に則して慎重に行う必要がある。