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Catalyst assisted destruction of trichloro ethylene and toluene in corona discharges

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Abstract: Destruction of trichloro ethylene (C_2HCl_3) by pulsed corona discharge reactor packed with alumina pellets and in absence of packing was investigated. Higher conversion of C_2HCl_3 was observed in presence of alumina than in absence of packing. Furthermore CO/CO_2 ratio in the by-products was found to shift in favor of CO_2 by alumina compared with absence of packing. Influence of catalyst porosity on C_2HCl_3 destruction and on by-product ozone generation during the processing was also studied. Both alumina-I and alumina-II show similar improvement in C_2HCl_3 destruction. However, more important observation was that alumina-I produces higher by-product ozone, while, alumina-II produces lower by-product ozone, than in the case of no packing. The catalyst porosity effect was also investigated for destruction of toluene and was found to be similar. Intermediates of C_2HCl_3 destruction, as identified by GC-MS, were $COCl_2$, $CH_2Cl_2CHCl_3$, CCl_4 and C_2HCl_5 . In presence of alumina the amount of these intermediates was much reduced, indicating the catalytic function of alumina.

Key words: corona discharges; plasma; trichloro ethylene; toluene; alumina

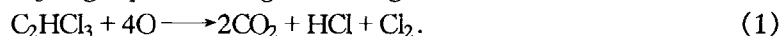
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Introduction

Trichloro ethylene is a very effective solvent to remove oil from silicon and other materials used in semiconductor industry. The C_2HCl_3 is one of the factors in producing high ground level ozone and is also found to be one of the carcinogens (Arno, 1996). Therefore it is mandatory to investigate the ways for effective destruction of C_2HCl_3 .

Recently destruction of C_2HCl_3 has been investigated using a number of non-equilibrium plasma techniques, e.g., electron beam (Koch, 1995; Vitale, 1997), pulsed corona (Futamura, 1997), ferroelectric packed bed corona (Futamura, 1997), silent discharge (Evans, 1993), surface discharge (Oda, 1996), and surface wave plasma reactors (Arno, 1996). The common principle of these non-equilibrium plasma techniques is based on energization of electrons by electrical energy while keeping the ambient gas molecules close to room temperature. The energized electrons, upon inelastic collision with ambient gas molecules, produce chemically active species such as O , O^- , O_2^+ , O_2^- , O_3 , OH , OH^- , N_2^* (* indicates activated state), secondary free electrons (e) and so on (Naidis, 1997). The energized electrons and the chemically active species react with the volatile organic compounds (VOCs) and result the harmless products. These techniques are energy efficient because the energy losses in heating up the ambient gas are minimized.

Corona discharge reactors are particularly attractive because of their technological simplicity, and the operation under mild condition. The corona reactor is efficient in producing atomic oxygen from air, that reacts with C_2HCl_3 in gas phase through following overall reaction (Evans, 1993).



The products HCl and Cl_2 can be easily removed by water spray or bubbling, while CO_2 is harmless

and can be emitted into atmosphere. However the stoichiometry of reaction (1) is difficult to achieve. Especially under the poor decomposition conditions, intermediates may appear in the exhaust stream and may even need second stage treatment (Futamura, 1997; Oda, 1996). Therefore there is a need to further improve the destruction efficiency for VOCs and to have a better control over the by-product selectivity in corona reactors. Recently surface mediated/catalytic reactions in the corona discharge reactors are being looked for to achieve these targets (Yamamoto, 1996; Malik, 1998; Jiang, 1998). Here a comparison of C_2HCl_3 destruction in pulsed corona reactor in presence and absence of alumina is presented. Effects of alumina on by-products selectivity and influence of alumina porosity on C_2HCl_3 destruction are discussed. The porosity effects for destruction of $C_6H_5CH_3$ are also studied to prove the validity of the findings for other VOCs.

1 Experimental

The apparatus and experimental procedure were the same as described earlier (Malik, 1998). The VOCs laden air was fed to the reactor at $400\text{ cm}^3/\text{min}$ flow rate. The reactor composed of earthen steel cylinder (24 mm ID and 230 mm length), with $4\text{ mm} \times 4\text{ mm}$ steel rod as high voltage electrode. High voltage pulses of 45 kV (positive polarity), $4\text{ }\mu\text{s}$ width, $0.4\text{ }\mu\text{s}$ rising time, were delivered to the reactor from pulse generator. Power reading from DC source was 7.4 W for all the experiments.

Pore size distribution of alumina pellets (spherical, 2–4 mm diameters) was analyzed by AUTOPORE II 9220 Mercury Porosimeter from Micromeritics. Concentrations of VOCs at reactor inlet and outlet were analyzed by GC (1102G), equipped with OV-17 column (3m ID, 2m length) and flame ionization detector. The intermediates of C_2HCl_3 decomposition were identified by FINNIGAN SSKU-700 GC-MS with OV-17 capillary column of 20m length. For GC-MS analysis the inlet concentration of C_2HCl_3 was set at $\sim 45\text{ }\mu\text{mol/L}$. Partial conversion under the set conditions seems to be optimum for identifying whole range of long lived intermediates. The CO and CO_2 at reactor outlet were separated on a 601 carbosphere column in GC 102G-D, converted to methane with a special methanizer, and were analyzed by flame ionization detector. Ozone at reactor outlet was analyzed by standard analytical procedure (Malik, 1998; Snell, 1972).

2 Results and discussion

The destruction of VOCs in corona reactors is dependent on pulse rise time, pulse peak voltage, pulse frequency, flow rate of the feed gas, inlet concentration of VOCs, and so on (Yamamoto, 1992; Nifuku, 1997). In the present study inlet concentration of the VOCs was selected as variable, keeping all other parameters as constant. One set of experiments was run with alumina-I, one with alumina-II packed in the discharge gap, and one, for comparison, was run under identical conditions without any packing. The surface area and pore volume data for alumina packing are given in Table 1, and pore size distribution curves are illustrated in Fig.1. The destruction results for C_2HCl_3 and $C_6H_5CH_3$, illustrated in Fig.2a and 2b respectively, show that both alumina-I and alumina-II clearly enhance the destruction efficiency.

The intermediates of C_2HCl_3 destruction, as identified by GC-MS analysis, are given in Table 2. Plausible decomposition mechanism for C_2HCl_3 , as described in literature (Koch, 1995; Vitale, 1997; Futamura, 1997; Evans, 1993), can explain the formation of these intermediates. Same

intermediates in presence of alumina and in absence of packing indicate similar decomposition mechanism in the two cases. However presence of alumina seems to force the destruction of C_2HCl_3 , and its decomposition intermediates, more towards completion. In separate experiments, similar enhancement in destruction of CCl_4 , $CHCl_3$, and CH_2Cl_2 (intermediates of C_2HCl_3 destruction), was observed in presence of alumina. These results corroborate the conclusion that alumina packing seems to play catalytic role in destruction of these intermediates.

Table 1 Porosity data for alumina-I and alumina-II packing

	Pore diameter, μm	Pore type	Surface area, m^2/g	Pore volume, cm^3/g
Alumina-I	>0.05	Macro-pores	~ 10.0	~ 0.4
	<0.05	Meso-, and micro-pores	~ 10.5	~ 0.02
	Total (all pores)		20.5	0.42
Alumina-II	>0.05	Macro-pores	~ 1.4	~ 0.12
	<0.05	Meso-, and micro-pores	~ 93	~ 0.12
	Total (all pores)		94.4	0.24

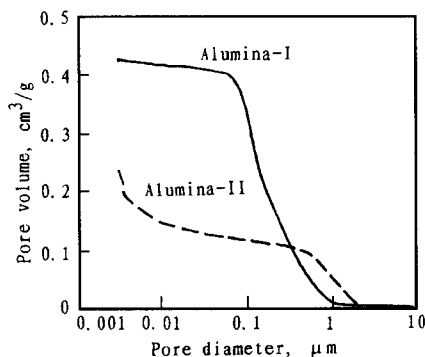


Fig.1 Pore size distribution curves for alumina-I and alumina-II

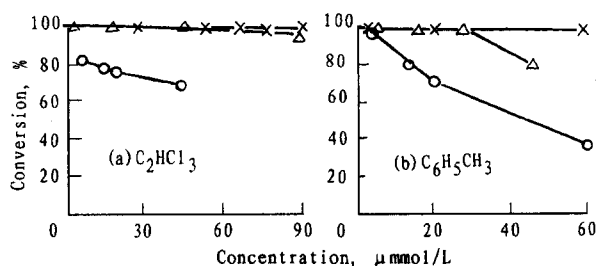


Fig.2 Inlet VOCs concentration vs. conversion curves in presence of alumina-I (\triangle), alumina-II (\times), and in absence of any packing (\circ) in pulsed corona discharge reactor

The CO/CO_2 ratio in the by-products was found to shift in favor of CO_2 by reducing inlet concentration of C_2HCl_3 , as shown in Fig.3. The shift in CO/CO_2 ratio correlates well with increase in C_2HCl_3 conversion at its lower inlet concentration as presented in Fig.2a. Similarly more CO_2 than CO was found in presence of

alumina than in absence of any packing. These observations further confirm the fact that alumina packing increases the oxidation potential in the corona reactor environment.

Because of high dielectric constant of alumina, electric field enhancement can result in higher energization of free electrons and production of more free radicals. Active plasma zone is limited to

Table 2 Intermediates of C_2HCl_3 decomposition identified by GC-MS

No.	Intermediate	No packing Peak height	Alumina-I Peak height
1	$COCl_2$	2.328×10^5	2.267×10^3
2	CH_2Cl_2	2.250×10^5	3.456×10^5
3	$CHCl_3$	4.952×10^4	6.400×10
4	CCl_4	1.109×10^4	6.800×10
5	C_2HCl_5	1.173×10^4	4.900×10

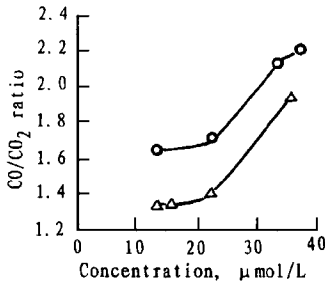
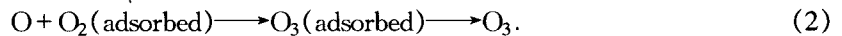


Fig. 3 The CO/CO₂ ratio during trichloro ethylene destruction in presence of alumina-I (—△—), and in absence of any packing (—○—) in pulsed corona discharge reactor

small regions of plasma channels (streamers), in absence of packing. In presence of packing the spread of active plasma zone, through micro-discharges at each pellet contact point, can be a factor in enhancement in VOCs destruction. Concentration of the VOCs in discharge gap, through adsorption, and consequent increase in its retention can explain the improved destruction efficiency in presence of alumina packing. Destruction of adsorbed VOCs and release of products may regenerate the active site (for next cycle of adsorption and destruction). Furthermore there is a possibility that some chemical bonds in the adsorbed molecule may be activated (Cordi, 1996) and become an easier target for plasma produced chemically active species.

During destruction of C₂HCl₃, and C₆H₅CH₃, the ozone concentration for different packing was in the following order: alumina-I > no packing > alumina-II, as illustrated in Fig. 4a, and 4b. The trend was, in general, similar for other VOCs. It can be explained on the basis of proposed ozone generation mechanism in presence of catalytic packing (Szalowski, 1996):



In reaction (2) solid surface acts as third collision partner and enhances overall ozone generation. The O, needed in reaction (2), is short-lived and consumed by a number of reactions. It is highly unlikely for O to diffuse into restricted regions, such as, meso- and micro-pores. Therefore, only macro-pores may show ozone generation activity. Higher macro-porous content of alumina-I explains its higher ozone generation activity. The ozone generation needs to be minimized in air cleaning application of corona reactors (Salam, 1997). Present finding provides a way to reduce by-product ozone without reducing the VOCs destruction efficiency of the catalytic packing by employing alumina-II.

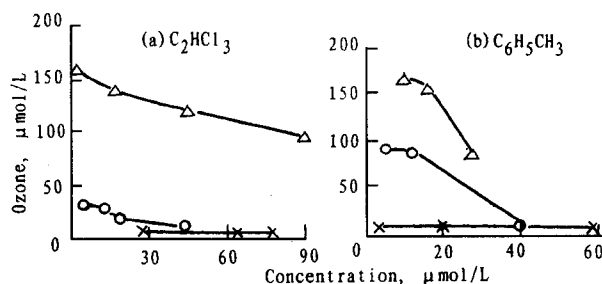


Fig. 4 Ozone concentration vs. inlet concentration of VOCs in presence of alumina-I (—△—), alumina-II (—×—), and in absence of any packing (—○—) in pulsed corona discharge reactor

Unlike the ozone generation activity, the VOCs destruction activity does not decrease in going from alumina-I to alumina-II. It may be attributed to the fact that the VOCs destruction is a complex process involving whole range of plasma produced chemically active species i. e., free electrons, free radicals, neutral molecules in activated state, neutral active species and probably also ionic species. Short-lived species, such as O, may destroy the VOCs in gas phase and on macro-

porous surfaces, while relatively long-lived species, such as O_3 , may diffuse into and destroy the target molecules in meso- and micro-porous regions also. Therefore meso- and micro-porous surfaces may also contribute, in some way or the other, to the C_2HCl_3 destruction activity.

3 Conclusion

Improvement in C_2HCl_3 destruction by packing the discharge gap of corona reactor with alumina pellets is clearly established. The packing also improves the removal of intermediates and provides control over the by-product selectivity, thus eliminating need for second stage treatment of by-products. Selecting the packing of higher overall surface area can lower ozone generation without affecting VOCs destruction efficiency.

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