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Destruction of VOCs by combination of corona discharge and catalysis techniques*

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Abstract—The catalytic effect of alumina on the destruction of toluene, benzene, acetone and methanol, in DC pulsed corona discharge reactor was studied. In the presence of alumina the inlet concentration of the VOCs was varied from $\sim 5 \times 10^{-6}$ mol/L to $\sim 80 \times 10^{-6}$ mol/L, and their decomposition efficiency (conversion %) was found to be 99%—80% for toluene, 99%—97% for benzene, 95%—92% for acetone, and 72% —85% for methanol. Corresponding decomposition in the absence of alumina was 90%—38% for toluene, 89%—57% for benzene, 42%—30% for acetone, and 47%—19% for methanol. Feed gas flow rate was 400 cm^3/min and power reading from DC source was 7.4 W in all of the experiments. Alumina also shifted the CO/CO_2 ratio in the by-products in favor of CO_2. Ozone concentration at the reactor outlet was higher in the presence of alumina. Enhancement in VOCs decomposition by alumina was explained on the basis of higher concentration of ozone and its precursor atomic oxygen [O]. Decomposition efficiency (conversion %) for individual compounds was found to be inversely proportional to the ionization potential of the compound, under identical conditions. Double DC high voltage sources pulse generator was tested and found to improve VOCs decomposition compared with the conventional single DC high voltage source.

Keywords: corona discharge; catalysis techniques; VOCs; decomposition efficiency.

1 Introduction

Volatile organic compounds (VOCs) are common air pollutants released from a number of industrial processes. The VOCs emissions are conventionally controlled by techniques such as thermal oxidation, catalytic oxidation, carbon adsorption, biofiltration, *etc*. (Cloud, 1996). Growing world's concerns for environmental protection has promoted testing and evaluation of a number of alternate techniques for abatement of VOCs (McInnes, 1995). Corona discharges are among the emerging techniques for destroying VOCs, which has been proven to be cost effective and environmentally friendly (McInnes, 1995; Yamamoto, 1992; Nunez, 1993). This technique is being tested at pilot plant in industrial scale (Connaughton, 1996; Pollution, 1996). In this technique electrical discharges are used to accelerate (heat up) electrons to very high energies, but, simultaneously, the rest of the gas stays at room temperature. The energized electrons attack the background gas molecules producing highly reactive radicals such as [O], [OH], [N], *etc*., that, in turn, decompose VOCs in air stream. The chemical reactions going on in corona discharge reactors are similar to those going on in thermal oxidizers, and the energy used in heating up the gas molecules in thermal oxidizers is saved.

There is intriguing possibility of catalytic reactions in corona discharge reactors (Kizling, 1996). Regarding the VOCs destruction, only one report in literature was found where active catalysts such as Co, Cu, Cr, Ni and V, impregnated on $BaTiO_3$ pellets, were employed for carbon tetrachloride (CCl_4) destruction, in corona discharge reactor (Yamamoto, 1996). A slight increase in destruction efficiency, along with higher conversion of by-product CO to CO_2, in presence of Ni

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catalyst was reported. Here we report the results of VOCs destruction in the presence of catalyst (alumina pellets), in pulsed corona discharge reactor.

2 Experimental

The alumina pellets of 0.2—0.4 cm diameter, 5—6 m^2/g surface area (BET), 0.4 cm^3/g pore volume (Mercury Porosimetry), and ~61% pores in the range of 100—410 nm diameter were used. The pellets were loosely packed in the reactor (Fig.1a). The alumina pellets were reused after oven treatment at 130℃ for ~6 hours. Air from air compressor was passed through silica gel, activated carbon and molecular sieve columns, successively, to remove impurities. Part of the pretreated air was bubbled through pure VOC in liquid state, placed in ice cold water bath. The VOC laden air was diluted with remaining air to a desired VOC concentration, and it was fed to the reactor at 400 cm^3/min flow rate.

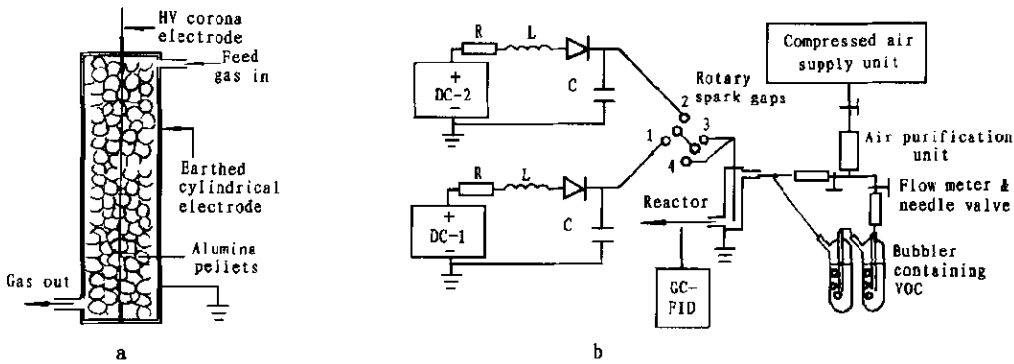

Fig.1 a: Reactor; b: DC pulsed power supply, feed gas supply and reactor assembly

The reactor was a stainless steel cylinder of 2.4 cm inner diameter (earthed electrode), with stainless steel corona electrode of 0.4×0.4 cm and 23 cm effective length, at the axis, and ~100 cm^3 volume. Principle parameters of pulse generator were: peak voltage value 0—45 kV (positive polarity) adjustable; pulse width 4 μs; rising time 0.4 μs; and repetition frequency 50—120 Hz. Schematic diagram of the whole assembly is illustrated in Fig.1. In the present experiments only one of the DC sources in Fig.1 (DC-1) supplied the power, and the other (DC-2 in Fig.1) was kept off (until mentioned otherwise). Power reading from DC source was 7.4 W, and voltage was fixed at 45 kV in all the experiments with single DC source. However a fraction of this power (~65%) is delivered in the discharge volume (Rea, 1995; Wang, 1995). The voltage pulse was delivered to the reactor when the rotating electrode connected position 1 and 3 in rotary spark gaps (Fig.1b). In some experiments (mentioned in text and figures) both DC sources, i.e., DC-1 and DC-2, supplied power ~7.4 W each. In the latter case voltage pulse was delivered to the reactor from DC-1 when the rotating electrode connected position 1 and 3, and from DC-2 when it connected position 2 and 4 in the rotary spark gaps (Fig.1b).

The concentration of VOCs at the inlet and outlet of the reactor was analyzed by GC-FID technique. The CO and CO_2 at reactor outlet were separated on a 601 carbosphere column, converted to methane with a special methanizer, and were then analyzed by FID (102G-D). The equilibrium VOC concentration at outlet was reached in ~15 min in the case of absence of catalyst. In the presence of catalyst the equilibrium was reached in ~120 min. All readings reported here

were recorded after establishing equilibrium. The decomposition efficiency was measured in terms of conversion % calculated by the formula:

$$\text{Conversion } \% = ((C_{\text{inlet}} - C_{\text{outlet}})/C_{\text{inlet}}) \times 100,$$

where C_{inlet} is the VOC concentration at inlet, C_{outlet} is the VOC concentration at outlet.

Ozone (O_3) at the reactor outlet was analyzed by standard analytical procedure (Snell, 1972). The sample gas was passed through an absorbent solution (2% KI and 0.4% NaOH in deionized water, used ~4 times in excess than required) for a known interval of time(10—20 min). After that added ~10 drops H_2O_2 solution (1 part of 30% H_2O_2 in 29 part water), boiled to expel excess H_2O_2, cooled back to room temperature, and adjusted pH to ~3.8 by 1:5 acetic acid in water. The liberated iodine was titrated against standardized $Na_2S_2O_3$ solution (0.005 mol/L). Ozone concentration was calculated using the formula:

$$\text{Ozone (mol/L)} = (A \pm B)M/V,$$

where A is the volume of $Na_2S_2O_3$ solution used (cm^3), B is the volume of $Na_2S_2O_3$ solution used during blank run (cm^3), M is the concentration of $Na_2S_2O_3$ (mol/L), V is the sample volume (cm^3).

3 Results and discussion

The decomposition (conversion %), both in the presence and absence of alumina, for toluene, benzene, acetone and methanol are plotted against the inlet concentration in Fig.2. In these experiments power from DC source was 7.4 W and gas flow rate was 400 cm^3/min. In order to increase (double) the applied power, double DC sources were used in some experiments. Under the double DC sources the decomposition for toluene in the absence of alumina, and for benzene in the presence as well as in the absence of alumina, is illustrated in Fig.2a and Fig.2b respectively. In these experiments the power from each DC source was 7.4 W, and the gas flow rate was 400 cm^3/min.

From Fig.2 it is observed that VOCs decomposition efficiency decreases with increase in VOCs inlet concentration, which is in accordance with literature (Yamamoto, 1992). Fig.2 clearly illustrates the higher VOCs decomposition in the presence of alumina, under all the conditions studied. In the presence of pellets of high dielectric constant material, such as alumina dielectric constant ~11 (Lide, 1993), partial corona discharges are produced at each pellet contact point, that spreads over the reactive zone in the whole reactor volume. High dielectric constant of the pellet material also enhances the electric field in the void spaces, that result in more acceleration of electrons (Yamamoto, 1992; Nunez, 1993). Furthermore, alumina being an adsorbent for VOCs (Goss, 1996), retains VOCs in the reactor for longer time through adsorption. High dielectric constant of alumina and its adsorption properties are factors influencing the enhancement of VOCs decomposition. In our preliminary tests we found that silica gel (adsorbent for VOCs) does not show such enhancement in VOCs decomposition. Studies reported in literature using ZrO_2 (dielectric constant ~ 12.5) for CCl_4 decomposition (Tonkyn, 1996) do not show such enhancement in decomposition. Therefore the factors described above, i. e., high dielectric constant and adsorption properties of alumina, are not thought to be the primary reasons for enhancement in VOCs decomposition. The most likely reason for better performance of alumina regarding VOCs decomposition is the catalytic generation of some reactive species that react with and destroy VOCs.

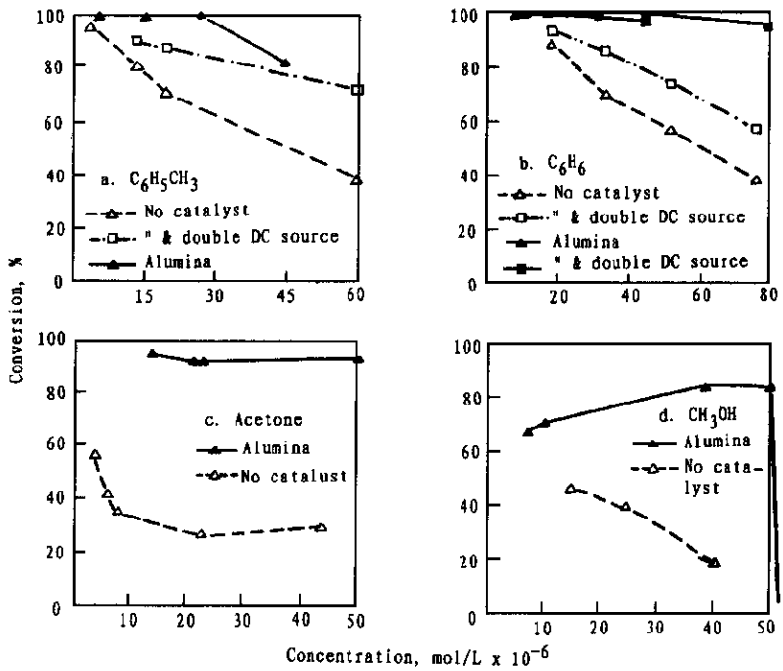

Fig.2 Rate of destruction (conversion %) as a function of inlet VOCs concentration, in presence and absence of alumina, at 400 cm^3/min flow rate of feed gas, 45 kV peak voltage, 7.4 W from DC source, 7.4 W from each DC source in case of double sources

In the pulsed corona discharge reactors the VOCs are primarily decomposed by reactive radicals such as [O], [OH], [N], *etc*. Particularly in dry air atmosphere, [O] is thought to play a predominant role in VOCs destruction in the corona discharge reactors (Evans, 1993). The [O] produces ozone, which is a very strong oxidizing agent, second only to fluorine in oxidizing power. Ozone alone is also being considered for VOCs destruction (Shanbhang, 1996).

The ozone concentration at the reactor outlet was analyzed, and was found to be two times higher in the presence of alumina, i.e., $\sim 2\times10^{-4}$ mol/L compared with $\sim 1\times10^{-4}$ mol/L in the absence of alumina, under the same conditions (dry air feed at 400 cm^3/min flow rate, 7.4 W power and 45 kV DC source voltage). Under different inlet concentrations of toluene, the ozone concentration at the reactor outlet was higher in the presence of alumina than in its absence (Fig.3). The ozone generation behavior under different inlet concentration of other VOCs was, in general, similar to that of toluene. These results clearly indicate the catalytic function of alumina in ozone, and consequently [O] generation from molecular oxygen. It is also observed from Fig.3 that the ozone concentration decreases with increase in toluene concentration, which correlates well with decrease in rate of toluene destruction (Fig.2). Ozone and its precursor [O] are consumed in the oxidation of VOCs. Furthermore increase in the inlet concentration of VOCs may make the active sites on alumina less available to molecular oxygen for the catalytic generation of ozone. Consumption of ozone and its precursor [O], and reduced accessibility of active sites on alumina with increase in VOCs concentration are responsible for the decrease in ozone concentration.

From the above discussion it is concluded that, in the presence of alumina, higher rate of VOCs destruction is primarily caused by the catalytic generation of ozone and [O]. Possibility of

surface mediated reactions of the adsorbed phase VOCs with reactive species is not waved out. Alumina catalyses VOCs decomposition in the catalytic incinerators (Cordi, 1996). There is a strong possibility of similar catalytic reactions in corona discharge reactors.

It was observed that different VOCs decompose to different extent under identical conditions. Their chemical reactivity and decomposition mechanisms can explain this difference. Among the physical properties of the VOCs, the decomposition efficiency was found to be inversely proportional to the ionization potential (Fig.4), which is in accordance with the literature (Nunez, 1993). Enhancement in VOCs decomposition by alumina is clearly visible from Fig.4.

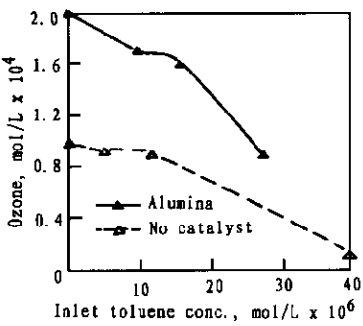

Fig.3 Ozone concentration as a function of inlet toluene concentration, in presence and absence of alumina, at 45 kV, 7.4 W from DC source, 400 cm^3/min flow rate of feed gas

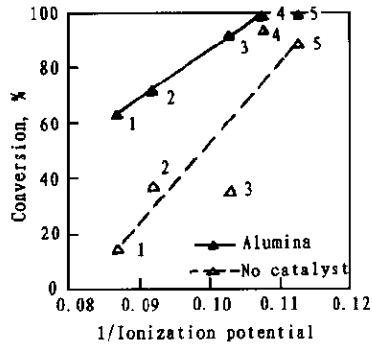

Fig.4 Conversion as a function of 1/(ionization potential), in presence and absence of alumina, at 45 kV, 7.4 W from DC source, 400 cm^3/min flow rate of feed gas, 8.93×10^{-6} mol/L inlet concentration of: 1 = carbon tetrachloride, 2 = methanol, 3 = acetone, 4 = benzene, 5 = toluene

Another important consideration regarding VOCs destruction is the control of by-product selectivity. In the present study CO/CO_2 ratio at reactor outlet, both in the presence and the absence of alumina, was analyzed under different inlet concentration of toluene (Fig.5a) and benzene (Fig.5b). It is observed from Fig.5 that with increase in inlet VOCs concentration the CO/CO_2 ratio shifts in favor of CO. This observation indicates that under the conditions of incomplete oxidation (destruction) of VOCs more CO is produced than CO_2. This fact correlates well with the decrease in VOCs decomposition (Fig.2), and the decrease in $[O_3]$ concentration (Fig.3), along with the shift of CO/CO_2 ratio in favor of CO. It is also observed from Fig.5 that alumina markedly shifts the CO/CO_2 ratio in favor of CO_2, indicating deep oxidation of VOCs, and corroborating catalytic function of alumina. Such trend of shift in CO/CO_2 ratio was, in general applicable to other VOCs also. Other by-products were not detected in the GC-chromatogram in the present study. However it is expected that alumina can catalyze the destruction of other by-products to harmless final products just as it does for the original VOCs.

In the pulsed corona reactors, the VOCs decomposition can be improved by decreasing inlet concentration of VOCs, by decreasing the flow rate of feed gas, and by increasing the power delivered in the reactor (Yamamoto, 1992; Munez, 1993). A new technique of employing two DC sources in the pulse generator was tested. The purpose was to increase (double) the power delivery into the reactor. Voltage pulse from one DC source may also provide DC bias voltage for the next voltage pulse from alternation DC source. This kind of self-imposed DC bias voltage characteristics of the pulse generator is known to be beneficial regarding the air pollutant destruction (Wang,

1995). Comparison of destruction efficiency for toluene, and benzene with double (DC-1 7.4 W, DC-2 7.4 W) and single (DC-1 7.4 W) DC sources is illustrated in Fig.2, at 400 cm^3/min flow rate of feed gas. Employment of double DC sources improves the VOCs decomposition. Especially the reactor containing alumina and equipped with double DC sources (Fig.2b) was found to decompose benzene almost completely in a wide range of its inlet concentration. Employment of double DC sources also shift the CO/CO_2 ratio in favor of CO_2 (Fig.5b) compared with the case of single DC source. Production of more CO_2 than CO confirms deep oxidation of VOCs.

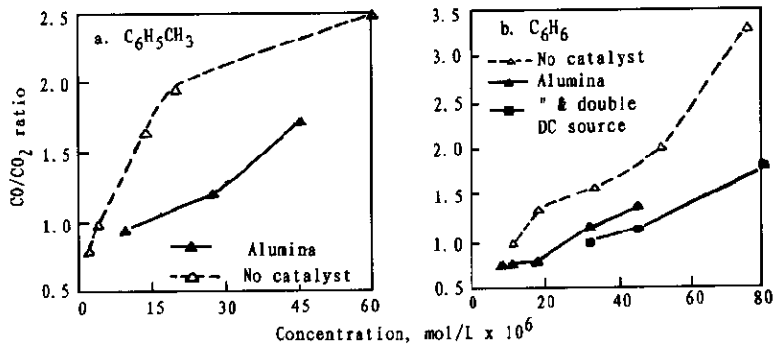

Fig.5 The CO/CO_2 ratio as a function of inlet concentration, in presence and absence of alumina, at 400 cm^3/min flow rate of feed gas, 45 kV peak voltage, 7.4 W from DC source and 7.4 W from each DC source in case of double sources, for (a) toluene and (b) benzene

Employment of catalyst (alumina) and double DC sources provide new tools for controlling VOCs emission by corona discharge techniques, and also improve the omnivorous nature of the reactors. The catalyst has been in use for ~6 months, and in this time no damage to the catalyst material was observed. Furthermore the enhanced generation of [O], and ozone in the presence of alumina can find application in commercial ozonizers, and in abatement of acid gases, i.e., SO_x, NO_x and so on.

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