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ABATEMENT OF FORMALDEHYDE BY STREAMER CORONA DISCHARGE COMBINED WITH CATALYST

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Summary: Abatement of formaldehyde by streamer corona discharge in multi point-to-plane reactor was studied experimentally. The removal efficiency of formaldehyde and the formation of products were evaluated as a function of the input concentration, the gas flow rate, the discharge polarity and mode. In addition, the effect of various pellet catalysts placed inside the discharge reactor was investigated. The chemical process and formed products were influenced by the processes of adsorption and plasma-assisted catalytic reactions. An improvement of the removal efficiency was observed with TiO_2 and γ-Al_2O_3 catalysts, especially at relatively high input energies and long-term operation.

Key words: corona discharge, formaldehyde, catalyst

1 Introduction

The treatment of various organic compounds in both air and water received much attention in the recent years. One of the most common organic compounds and major indoor air pollutant is formaldehyde, which is used in building materials such as plywood, chipboard and paneling. It can also be found in tobacco smoke and emissions from gasoline motor vehicles. The abatement of formaldehyde from indoor air can be achieved by using adsorbents, such as activated carbon, ceramic porous materials or composite oxidized catalyst [1-2]. Another alternative, often used for the abatement of various volatile organics is non-thermal plasma generated by electric discharges. The chemical effect of the plasma can be enhanced if it is combined with catalyst [3-5].

In this paper, the abatement of formaldehyde and formation of products in air and nitrogen mixtures by d.c. streamer corona discharge was investigated. The effects of input concentration, gas flow rate, discharge polarity and mode are reported. The combination of the discharge plasma assisting the processes occurring on the catalysts placed in the discharge volume was examined.

2 Experimental Set-up

The experimental set-up is depicted in Fig.1. Discharge reactor of multi point-to-plane configuration was used, with plane electrode perforated. The distance between the electrodes was 16 mm. The discharge was driven by a stabilized d.c. power supply. In the experiments with catalyst, a layer of catalytic pellets was placed on the plate electrode. The height of the layer was 8mm. Investigated catalysts

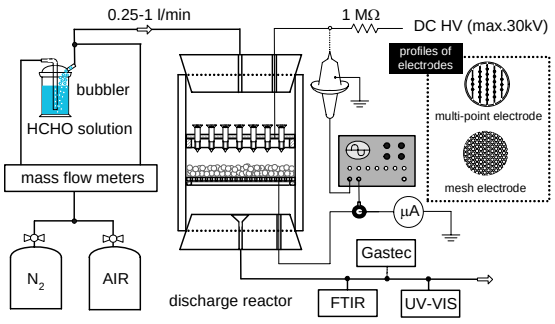

Figure 1: Experimental set-up

were TiO_2, Pt/Al_2O_3, γ-Al_2O_3, molecular sieves 13X and sodium zeolite LZ-Y54. Formaldehyde vapors (190-1220 ppm) were produced by bubbling air or nitrogen through a solution of formaldehyde (containing 5% of methanol as a stabilizer). The total gas flow rate was controlled by the mass flow meters and the experiments were carried out at the room temperature. The analysis of the gas composition was performed by the infrared spectrometry.

3 Results

The removal efficiency of formaldehyde (%) for a given specific input energy (SIE, J/l) was found to be higher for smaller initial concentrations of formaldehyde (within the range of 190-1200 ppm). Figure 2 shows the removal efficiency as a function of SIE in air or nitrogen as the carrier gas. For the given SIE, the energy consumption (eV/molecule) is smaller for higher initial concentrations of formaldehyde. For example, in the presented Fig. 2 at the specific input energy of 100 J/l and the initial concentrations 190 ppm and 1220 ppm in air, the achieved energy consumption were 131 and 68 eV/molecule, respectively.

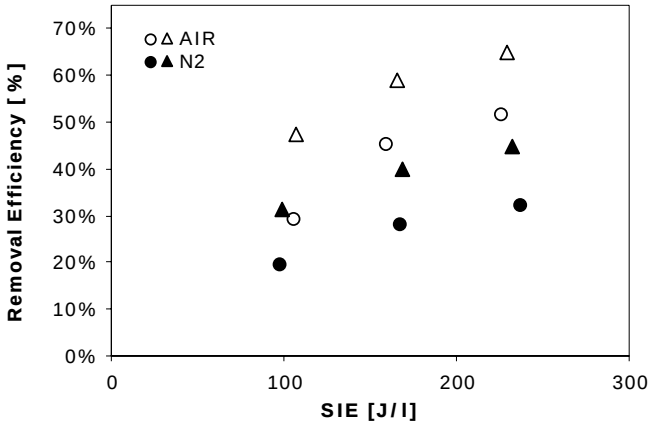

Figure 2: Removal efficiency of formaldehyde treatment – air: △ 190, ○ 1220 ppm; nitrogen: ▲ 190 ppm, ● 1200 ppm HCHO; 1.0 l/min.

The main products of formaldehyde decomposition are carbon oxides CO and CO_2 and formic acid HCOOH. The formation of CO occurs either directly through photolytic reaction ($HCHO + h\nu \rightarrow CO + H_2$), or indirectly via intermediate HCO radical, followed by the reaction with oxygen ($HCHO + h\nu \rightarrow H + HCO$, $HCO + O_2 \rightarrow CO + HO_2$). The second pathway is important for oxygen containing mixtures. Carbon monoxide can be further oxidized to carbon dioxide, mainly by OH radicals. The formation of HCOOH occurs most probably though oxidation of formaldehyde by oxygen radicals ($HCHO + O \rightarrow HCO + OH \rightarrow HCOOH$). The reaction with ozone, however, is not effective ($HCHO + O_3 \rightarrow HCOOH + O_2$). Due to the existing oxidation process, the removal is higher in air, than in nitrogen, which was also confirmed by the experimental results.

Figure 3 shows differential infrared absorption spectra (spectrum of the input gas is subtracted from the output gas) of formaldehyde abatement by the streamer discharge of the positive polarity in two different carrier gases. Apart from the main products, there are several other minor products identified in the output mixture. For example, methyl formate $HCOOCH_3$ and other compounds containing methoxy group CH_3O, which result from formaldehyde and methanol decomposition. In oxygen free mixtures, small concentration of

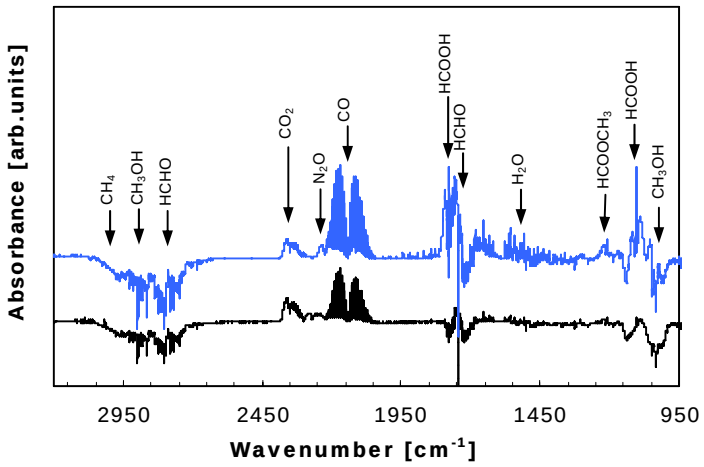

Figure 2: Differential spectra of formaldehyde abatement by d.c. corona discharge in air (up) and nitrogen (down) carrier gas; 1220 ppm HCHO, 0.5 l/min, SIE 300 J/l.

methane CH_4 was found as the result of the reduction process. Formation of ozone and limited amount of NOx was observed in air.

The results also showed that the removal efficiency of formaldehyde at the given specific input energy was found higher for higher gas flow rates (within the range of 0.25-1.0 l/min). The efficiency depends also on the used discharge polarity and mode. Direct comparison of the results obtained with different polarities is, however, complicated due to different dominant discharge modes (glow corona in negative, streamer corona in positive). The production of active species and oxidants (e.g. O, O_3) at the given SIE is much more efficient in the streamer mode than in the glow mode. Therefore, the removal of formaldehyde in positive polarity is more efficient. The efficiency rapidly decreases upon the streamer transition to spark. The spark decreases CO and HCOOH production and increases CO_2, NO and NO_2 production.

A layer of catalyst consisting of pellets of various materials and properties (TiO_2, Pt/Al_2O_3, γ-Al_2O_3, molecular sieves) was placed on the plate electrode to support the plasma chemical process of formaldehyde abatement. The effect of the catalyst on the removal of formaldehyde and formed products has been investigated without or with plasma. Adsorption, absorption, photocatalytic and surface oxidations were the processes expected to play important roles.

The concentration of formaldehyde was reduced by the absorption on the catalytic pellets even without discharge. At the reactor output, the formaldehyde concentration was first very small (few % of the input), slowly increasing in time and saturating after several hours, usually 12 or more. The concentration saturated either at the level bellow the input concentration (less than 50% of the input for LZY-54, γ–Al_2O_3, Pt/Al_2O_3) or almost reached this level (89% for TiO_2). By comparing the absorption spectra of the input and output gas mixtures after several hours, various effects were observed. For γ-Al_2O_3, 13X and LZ-Y54, a partial removal of formaldehyde and methanol without formation of any gaseous product (e.g. CO, CO_2, HCOOH) was observed indicating important role of the adsorption. For Pt/Al_2O_3, significant decrease of formaldehyde concentration was observed, accompanied by the production of carbon dioxide CO_2 and methyl formate $HCOOCH_3$ indicating the effective oxidation at the catalyst surface. At last, TiO_2 showed minimal absorption abilities.

The experiment of formaldehyde abatement by corona discharge with catalyst has been carried out for several hours (4-5 hours) at the specific SIE. When comparing different catalysts, the relative improvement of removal efficiency was observed especially at higher SIE.

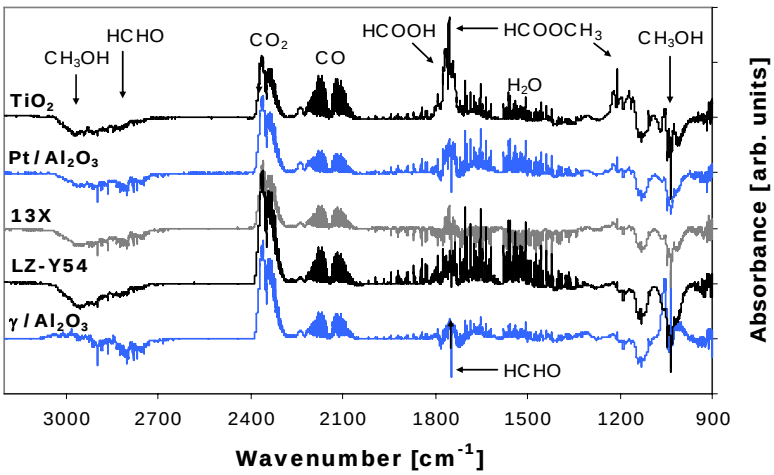

Figure 4: Differential spectra of formaldehyde abatement with selected catalysts with discharge after 150 min (230 ppm, 270 J/l, 1.0 l/min).

With SIE > 300 J/l, the achieved treatment efficiency of plasma-catalyst system was generally better than using either catalyst or plasma alone (e.g. γ-Al_2O_3, TiO_2). Figure 4 presents the differential spectra of gas mixtures treated with discharge plasma and catalyst. Similar to the treatment with plasma alone, the formation of CO and CO_2 is dominant. The difference is smaller amount of HCOOH and O_3 produced by plasma with catalyst. For TiO_2, the removal of HCHO was improved if compared either with plasma or catalyst alone treatment. The products of the abatement were CO, CO_2 and HCOOH. In addition, the ester $HCOOCH_3$ was found in as the product, which concentration was highest among the used catalyst. Several other effects were observed for other catalysts. For example, a significant absorption of water vapors with 13X, the highest concentration of water vapors with LZ-Y54, the effective oxidation of methanol for all catalysts, etc.

4 Conclusions

The abatement of formaldehyde in air and nitrogen by streamer corona discharge combined with catalyst was investigated. Removal efficiency increased with the initial concentration of formaldehyde and decreased with the gas flow rate. An improvement was observed when TiO_2 and γ-Al_2O_3 catalysts were present inside the discharge reactor, especially at higher SIE and long-term term operation. The formation of products depended on the used catalyst.

Acknowledgement

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