Report on Visit to Bari University by International Training Program

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As a long-term placement program of ITP (International Training Program, I had studied in the Prof. Fracassi research group in Bari University of Italy for three months, from November 19, 2012 up to February 24, 2013. This is a report of my stay.

Research

(a) Research theme

The research theme is devoted to the volatile organic compound (VOC) abatement using a dielectric barrier discharge (DBD) coupled with a catalytic system. Among the most innovative techniques for VOC abatement, atmospheric pressure plasma have been found to be one of the most convenient for low concentration of pollutant (usually 1000 ppm).[1] These plasmas have been used not only for the VOC oxidation but also SO_x and NO_x reduction, even if the poor selectivity towards complete oxidation and the formations of dangerous byproducts are the main drawbacks of these processes.[2] To overcome these problems, atmospheric pressure plasmas are often coupled with other depollution techniques as scrubbers [3] or catalytic systems.[2] According to the location of catalyst, the plasma catalysis system scan be divided in two categories.[4]

- Plasma driven catalysis, in which the catalytic material is inserted into plasma region to produce a mutual effect of plasma and catalytic material. In fact, the short-life reactive species produced in the plasma can induce an increase in the work function of the catalyst and enhance the reduction of active metals, promoting oxidative reactions. The presence of packing material in the plasma region, instead, enhances the electric field strength and thanks to adsorption phenomena, increase the retention time of the pollutants in the plasma region;
- Plasma assisted catalysis, in which the catalytic material is generally placed downstream from the plasma region. The byproducts generated in the discharge can be used to oxidize further the organic compounds at a lower temperature respect to mere catalytic abatement. Two kinds of catalyst are generally used for this application: noble metal-based catalyst and metal oxide-based catalyst. The further are really efficient in increasing the selectivity towards CO_2, even if they work at very high temperature and if they are poisoned by CO. The latter are less expensive even if less efficient respect to noble metal catalyst but have a lower working temperature and could be less subjected to poisoning.

In this study, a DBD reactor with a coaxial geometry was used. A catalytic reactor was placed downstream respect to the DBD. The studied VOC was 2-hexanone which has never been studied. 2-hexanone is a pollutant that could be present in the air close to industry or hazardous waste site that releases the liquid into wastewater or the gas form into the surrounding air. The most important health concern for humans from exposure to 2-hexanone is its harmful effects on the nervous system, causing weakness, numbness, and tingling in the skin of the hands and feet.

(b) Experimental

The experiments started to investigate the effect of different metal loading supported Mn oxide catalyst on the performance of the hybrid system. I used Mn based catalyst supported on γ-Al_2O_3. The experiment proceeded according to the following steps:

- Sampling procedure optimization and evaluation of the stability and the reproducibility of the measurements;
- Analysis of the exhaust obtained from the air/2-hexanone plasma followed by the catalytic treatment at 200 °C;
- Comparison of the results with those already obtained without catalyst

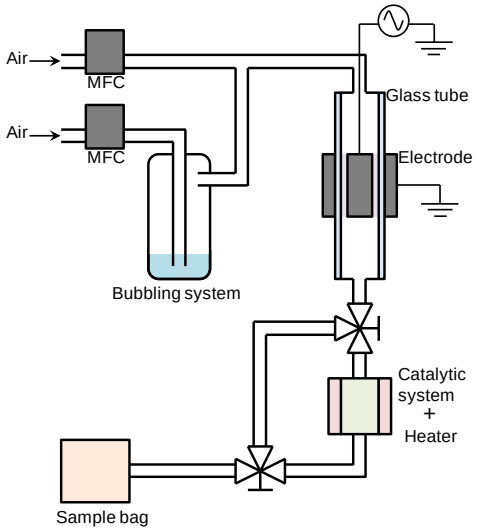

Figure 1. Schematic of experimental setup.

The schematic of experimental setup is shown in Fig. 1. VOCs are added to the feed gas by bubbling an air flow into a VOC reservoir. Plasma is generated by applying high-voltage pulsed signal ($V_{p\text{-}p}$: 17.0 kV, Duty cycle: 20 %, t_{ON}: 1.17 ms). Total gases flow rate was 1000 sccm (combined value of main air flow and bubbling system flow). The catalytic system is heated at 200 °C. The power dissipated in the plasma is approximately 4.5 ± 0.1 W.

The exhaust gas is collected in a sampling bag, in which a fixed amount of an internal standard (C_6F_{14}) is inserted. The collected sample is analyzed by GC-MS to quantify the remaining VOC and some organic byproducts. The quantification of organic species is obtained by dividing the peak areas of the analytes for the peak area of the internal standard. Calibration curves allow the absolute quantification of the analytes. Moreover, by using previously calibrated instruments, it is possible to obtain the direct measurement of [CO], [CO_2], [O_3], [NO] and [NO_2].

The GC-MS curves are built as injected mmol versus relative peak area (analyte peak area over internal standard peak area). The calibration curves are used to calculate the injected mmol of the analytes, that are converted in ppm_v using the following equation:

$$ppm_v = \frac{mmol \times 10^{-3} \times R \times T}{V_{inj}} \times 10^6$$

in which T equals to 273.15 K and the injected volume, V_{inj} equals to 1 ml.

Moreover, after the conversion of the relative areas in ppm_v, the depletion of 2-hexanone is calculated by using the following equation:

$$Depletion[\%] = \frac{ppm_{OFF} - ppm_{ON}}{ppm_{OFF}} \times 100$$

For every analyte, the obtained ppm_v are multiplied for the number of carbon atoms in the analyte to have a balance of total ppm_v of detected carbon, than all the organic carbon ppm_v are summed. The measured ppm_v of CO and CO_2 are also summed to calculate the carbon balance as

$$Carbon\ balance = \frac{C_{theoretical} - C_{measured}}{C_{theoretical}} \times 100$$

Fig. 2 shows the concentration of O_3 and NO_2 detected in the exhaust of the different tested systems using only air as feed gas. Without catalyst, there is a high production of O_3 and NO_2, while the NO is not revealed. This phenomenon can be explained by the fast oxidation of NO to NO_2 by O_3. As far as the catalytic material is inserted downstream from the reactor, a dramatic decrease of these species is measured. The best results are obtained for 5 % Mn-Al_2O_3 catalyst, that totally abates both O_3 and NO_x.

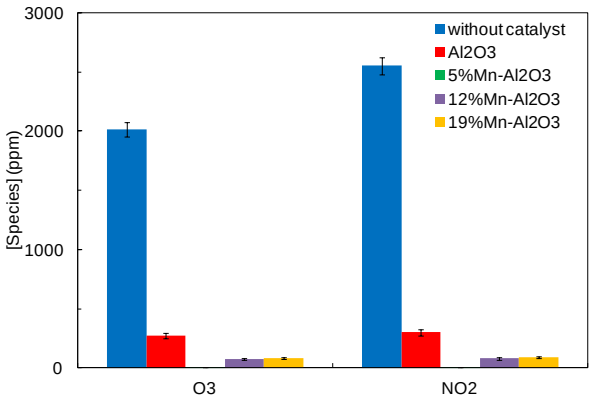

Figure 2. Byproducts in exhaust (Air plasma).

When 200 ppm of 2-hexanone are inserted into the feed gas, the organic radicals formed in the plasma region are able to decrease the level of O_3 and NO_2 produced. Also in this case, the concentration of NO is below the detection limit of the instrument. As it is shown in table 1 and 2, the amounts of these species are always lower respect to the air plasma

values. Moreover, the presence of catalytic material, further improve the performance of the system, by lowering the concentration of ozone and of NO2 to very low values, especially if Mn was added to the catalyst. The 5%Mn-Al_2O_3 catalyst gives the best results both in air than in air-VOC plasma, reducing both O_3 and NO_2 to values dose to zero.

Table 3 shows the depletion for 2-hexanone for the studied systems. It is evident that the use of a catalyst enhances the VOC abatement. There are no significant differences in the different loaded catalysts. However, non predictable adsorption and release phenomena cannot be excluded. These phenomena can affect the final value of the depletion. Further investigations are need to clarify these aspects.

Fig. 3 shows the quantified organic byproducts. The presence of catalyst not only increases the efficiency in the abatement but also decreases the concentration of species like acetone and formic acid in the exhaust. In particular, the use of Mn-based catalysts produces a very low quantity of these byproducts. The concentration of acetone in the exhaust of the system plasma+alumina is higher respect to the other system. This result could be explained considering that acetone could be one of the first steps of the 2-hexanone abatement and that alumina is not efficient enough in further oxidize this species. The catalytic material is, not effective in the reduction of methyl nitrates and acetic acid.

Table 1. O_3 concentrations.

Catalyst	O_3 [ppm]	
	Air	Air+2-hexanone
Without catalyst	2012 ± 61	1150 ± 18
Al_2O_3	273 ± 24	96 ± 37
5%Mn- Al_2O_3	8 ± 1	Not detected
12%Mn- Al_2O_3	76 ± 10	Not detected
19%Mn- Al_2O_3	81 ± 7	Not detected

Table 2. NO_2 concentration.

Catalyst	NO_2 [ppm]	
	Air	Air+2-hexanone
Without catalyst	2551 ± 73	1232 ± 58
Al_2O_3	303 ± 28	109 ± 16
5%Mn- Al_2O_3	8 ± 1	31 ± 1
12%Mn- Al_2O_3	81 ± 11	6 ± 1
19%Mn- Al_2O_3	90 ± 6	7 ± 3

Table 3. Depletion of 2-hexanone.

Catalyst	Depletion [%]
Without catalyst	82 ± 2
Al_2O_3	94 ± 1
5%Mn- Al_2O_3	96 ± 1
12%Mn- Al_2O_3	96 ± 1
19%Mn- Al_2O_3	94 ± 1

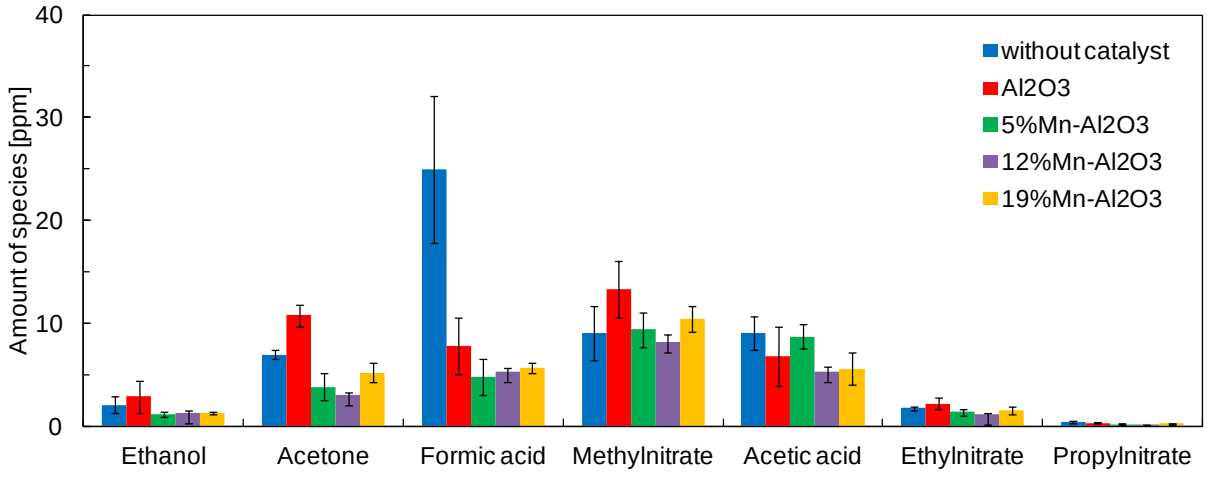

Figure 3. Organic compounds in exhaust.

Fig. 4 and 5 show results of measured carbon oxides in an air+2-hexanone plasma. The CO and CO_2 yields are increased at using catalysts. Adsorption and dissociation phenomena, involving both species like O_3 and NO_x and organic compounds, can push the oxidation of 2-hexanone towards carbon oxides. The total quantities of CO and CO_2 are approximately the same at each of catalysts, even if the CO_2/CO ratios are higher for 5 and 12%Mn-Al_2O_3. Therefore, CO_2 ratios increase with decreasing Mn loading rate. This effect could be due to the higher dispersion of Mn in the catalytic support that has been verified to be effective in enhancing the catalytic performance in VOC abatement. A deep characterization of the catalyst is needed to verify this hypothesis.

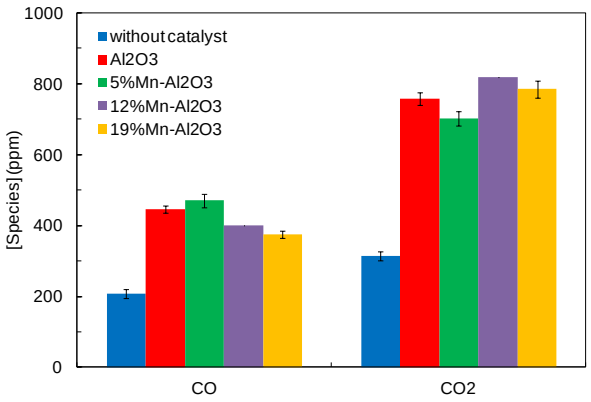

Figure 4. CO and CO_2.

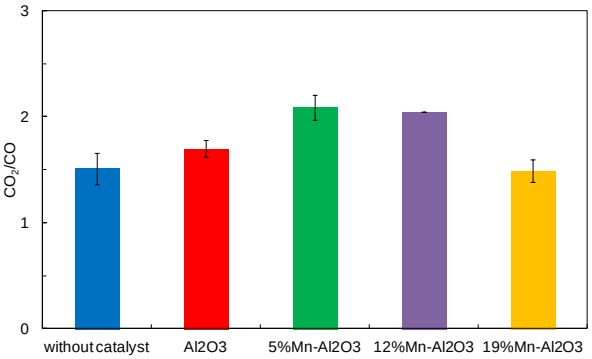

Figure 5. CO_2/CO ratio.

College life in Bari

It was 09:40 pm on November 19th when I arrived at the Bari airport. Bari University is located about 10 km away from the airport, it takes about 10-15 minutes by car. The accommodation I stayed is such as hotel for long-term residents, it is called CampusX. In the accommodation, I could use common wash machines, and bed sheets and towels changing each time I needed it. The restaurant is open, I was able to use every day.

University is located about 20 minutes on foot from the accommodation. There is also a complimentary shuttle service from the accommodation to University. Walking further 10 minutes from the University, I can reach downtown. In Italy, a lot of people are going out even after 8 pm because shops are open until late at night.

I often buy lunch at shop near University. I could eat fully satisfying about 3 Euros. After lunch, I always went to bar in University and drank espresso. Surprisingly, the price of a cup of espresso is 50 cents.

Summary

I had studied about the volatile organic abatement using a dielectric barrier discharge reactor coupled with plasma assisted catalytic system. I used γ-Al_2O_3 and different Mn loaded rates γ-Al_2O_3 as catalysts.

Plasma assisted catalytic system enable to reduce remaining 2-hexanone and byproducts (O_3, NO_2 and organic compounds) in exhaust. The best results are obtained for 5%Mn-Al_2O_3 catalyst, that totally abates both O_3 and NO_x. CO_2/CO ratio increase with decreasing Mn loading rate.

Finally, I deeply appropriate Prof. Fracassi, Prof. Hori, and Prof. Toyoda for giving me such a great opportunity, and all of people for assisting my stay.

References

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