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The effect of catalyst properties on tars removal by plasma catalysis

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Abstract: The paper deals with the removal of tars by non-thermal plasma generated by dielectric barrier discharge in combination with packing materials of various composition and catalytic activity (glass beads, γ-Al_2O_3 TiO_2, $BaTiO_3$, ZrO_2, Pt/γ-Al_2O_3), shape and size (∅ 2-5 mm) and specific surface area (35-250 m^2/g). The effect of the packing materials was investigated along with the effects of specific input energy and carrier gas, while gaseous and solid by-products were analysed by means of FTIR spectrometry.

Keywords: dielectric barrier discharge, plasma catalysis, naphthalene removal

1. General

A huge demand on environmentally friendly technologies for energy production other than conventional methods based on the combustion of fossil fuels led to a search for new alternative methods. A gasification of biomass and separated waste represents one of them, where the fuel is being converted into synthesis gas (syngas), i.e. a mixture of H_2, CH_4, CO and CO_2 that possesses high energy potential. The syngas produced by gasification however often contains various unwanted substances, e.g. particulate matter and tars, which must be removed before further utilization of the syngas. Tars in particular are associated with system malfunction, material corrosion, they block particle filter and deactivate catalysts. Therefore their removal from syngas represents a major challenge. Several commercial methods for tars removal exist with chemical catalytic decomposition being the most common one.

For several decades non-thermal plasma (NTP) processes have been studied and used in numerous environmental applications, mainly for air and water pollution control [1]. NTP can be generated by various atmospheric pressure discharges and is able to convert gas pollutants into harmless compounds. The removal of various hydrocarbons by NTP has been investigated by various research groups [2] with benzene and toluene being the most commonly used as target compounds. The NTP gas processing usually possesses decent removal efficiency, but has several disadvantages in low selectivity and high energy consumption, which limit its practical use. To overcome these disadvantages, a combination of NTP with catalysts seems to be a promising method that allows to utilize the individual benefits of the plasma and the catalyst [3], especially when the catalyst is placed directly in the plasma zone. Plasma catalysis is characterized by synergistic effects that are the result of the plasma–catalyst interaction and usually lead to stronger effects than the sum of the individual effects of plasma and catalyst alone.

Tars removal by the NTP has been studied by several research groups in recent years. The majority of these studies focused on their removal using various discharges (corona discharge, DBD or gliding arc discharge), gas temperature (200–500°C), gas composition (naphthalene, toluene, phenol, syngas) and discharge power. Although tars removal by NTP is quite well documented, its removal by a combination of NTP with catalysts in a plasma catalytic system have been reviewed only by few papers, with toluene being the most common target tar compound [4-6] and with Ni- or Fe-, MnO_2 being the most studied catalysts.

The objective of this work was to investigate tars removal by NTP generated by atmospheric pressure DBD in combination with packing materials of various composition and catalytic activity (glass beads, γ-Al_2O_3 TiO_2, $BaTiO_3$, ZrO_2, Pt/γ-Al_2O_3), various shape and size (beads and pellets, ∅ 2-5 mm) and various specific surface area (35-250 m^2/g). The packing materials were chosen for their different properties - glass beads as a dielectric material without any specific catalytic activity, γ-Al_2O_3 as being the most common bulk material for the supported catalysts, TiO_2 as the most common photocatalyst, $BaTiO_3$ as a perovskite photocatalyst with exceptionally dielectric constant, while Pt and ZrO_2 were chosen as being amongst the best catalysts reported for hydrocarbon removal. The effect of specific surface area was also examined, as it is known to be closely related with catalyst performance. Naphthalene was chosen as a model tar compound because it is the simplest polycyclic aromatic hydrocarbon and one of the most difficult tar compounds to decompose. In addition to the effect of packing materials on naphthalene removal, the effect of specific input energy and carrier gas were also investigated. In contrast to the existing works on naphthalene removal, we performed our experiments at a relatively low operating temperature (below 150 °C) and with relatively high initial concentrations (5000 ppm).

2. Experimental setup

NTP was generated by cylindrical geometry DBD reactor filled with various packing materials. The reactor was powered by an AC high voltage and operated in the streamer discharge mode with various specific input energies (SIE, up to 1000 J/L), in various carrier gases (ambient air, oxygen or nitrogen) and at the constant gas flow rate (0.5 L/min). Gaseous and solid by-products of naphthalene decomposition were analyzed by means of FTIR spectrometry. More details on the plasma reactor and the experimental setup can be found in [7].

3. Experimental results and discussion

Electrical measurements shown the SIE increased with the amplitude and the frequency of the applied voltage, while the effect of carrier gas and packing material on the SIE was very small or almost negligible, respectively.

Naphthalene removal efficiency (NRE) increased with the increase of the amplitude and frequency of the applied voltage. In the plasma catalytic reactors, higher NRE was achieved at lower SIE thus demonstrating the positive role of catalyst in the naphthalene removal process in comparison with plasma alone. The carrier gas had significant effect on the NRE, as different reactive species were formed. In nitrogen, species such as $N_2(A)$ or N dominates, while in oxygen it is rather $O(^3P)$, $O(^1D)$ and O_3. In ambient air, excited $N_2(A,B,C)$ supports formation of additional O, while residual humidity supports formation of OH. All these reactive species more or less effectively oxidize/reduce naphthalene molecules. In nitrogen, the NRE was very poor (<25%) with mono- and hetero- N-containing aromatic compounds being the main by-products. In ambient air, the NRE was significantly higher (up to 88%) and accompanied by the formation of CO/CO_2 and O-containing hydrocarbons or hydrocarbons with fewer carbon atoms. In oxygen, complete naphthalene removal was achieved due to improved oxidation governed by O and O_3.

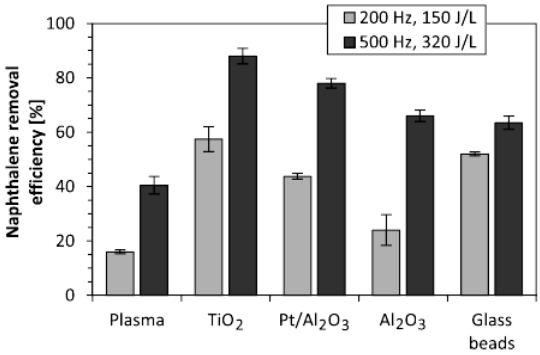

Fig.1. Effect of packing material on naphthalene removal efficiency in ambient air.

The effect of packing materials of various composition and catalytic properties (glass beads, γ-Al_2O_3 TiO_2, $BaTiO_3$, ZrO_2, Pt/γ-Al_2O_3) was examined. Figure 1 shows the NRE obtained in ambient air for selected materials at two different SIEs (150 and 320 J/L). The highest NRE was reached with TiO_2 catalyst (88%, 320 J/L), while the NRE with the Pt/γ-Al_2O_3 catalyst was only slightly lower, but shown much higher CO_2 production suggesting the best oxidation abilities compared to other materials. $BaTiO_3$ and ZrO_2 shown also relatively high NRE and their effects will be discussed in details during the symposium. Materials without specific catalytic properties, i.e. γ-Al_2O_3 and glass beads, showed smaller NRE, however still higher than a plasma reactor. The effect of the specific surface area of the packing material on the NRE was also examined. The surface area is known to affect the adsorption, catalyst performance and enhances discharge volume distribution. TiO_2 catalysts of three different surface areas in the range of 35-250 m^2/g were examined. Small improvement of the NRE was observed and will be presented in details during the symposium.

The main products of naphthalene decomposition were CO, CO_2, H_2O and HCOOH found in gas and solid by-products found on the walls of the reactor and on the packing material. Several absorption bands corresponding to functional groups, such as C=O, C=C, C–O, C=N, N–H or O–H were found and indicate the production of various hydrocarbons. The detailed analysis allowed us to identify 1,4-naphthoquinone and phthalic anhydride among the products, along with maleic anhydride, 1,4-benzoquinone and phthalaldehyde.

4. Conclusion

The effect of NTP in combination with various packing materials on tars removal was investigated. Naphthalene removal efficiencies (NRE) up to 88% and 100% were achieved in ambient air and oxygen, respectively. TiO_2 and Pt catalyst showed the highest NRE compared to other packing materials. Specific surface area and size of material played a minor role. CO, CO_2, H_2O and HCOOH were identified as by-products, as well as more complex compounds, such as 1,4-naphthoquinone and phthalic anhydride. The results proved, that combination of the non-thermal plasma with catalysis is very efficient method for tars removal that allows better efficiency compared to the non-thermal plasma alone treatment.

5. Acknowledgement

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