

Removal of Toluene in Air by Non Thermal Plasma-Catalysis Hybrid System

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Abstract: Atmospheric Non-Thermal Plasma (ANTP) technology for indoor air treatment has the disadvantage to produce undesirable by-products such as ozone and NO_x. To overcome the by-products formation and increasing energy efficiency, ANTP could take advantage of its synergetic effect through combination with heterogeneous catalysts. This combination can be either single-stage (in-plasma catalysis, IPC) or two-stage (post plasma-catalysis, PPC).

Various catalysts based on Ag, Au, Cu, Co, Mn, La (supported on OMS-2, Al₂O₃ or CeO₂) and Nb has been investigated with and without a dielectric barrier discharge (DBD). In the absence of catalysts, the toluene removal efficiency was about 60% with O₃, CO, CO₂, and NO_x as reaction products. Without plasma, the reaction of toluene conversion over Al₂O₃, OMS-2, and perovskite based catalysts are promoted only at high temperature (200-400°C).

When the plasma was combined to catalyst at room temperature, the toluene removal efficiency strongly increased when the catalysts are in IPC position. Best results, up to 96% toluene conversion, were obtained when using 1wt% Au/Al₂O₃ or Nb₂O₅ catalysts. The products of the toluene oxidation were CO and CO₂.

Keywords: Non thermal Plasma, Catalysis, Toluene, Oxidation.

1. Introduction

Volatile organic compounds (VOCs) are an important category of air pollutants and therefore, become a serious problem for damaging the human health and the environment in general [1, 2]. Well established technologies for VOC abatement are thermal and catalytic oxidation, adsorption, condensation, bio-filtration, membrane separation or UV oxidation [3, 4]. The thermal and catalytic methods, which are widely used, are very efficient to oxidize VOCs. However, these technologies which require a substantial supply of thermal energy (700-800°C for thermal incineration and 200-600°C for catalytic oxidation) are not well adapted and energetically expensive in the case of moderate gas flow rates containing low VOC concentrations. In addition, the catalyst poisoning followed by deactivation represents a serious problem for these technologies.

As an alternative to conventional VOCs abatement techniques, ANTP technology received increasing interest during the last decade for the removal of dilute VOCs from many sources. ANTPs for environmental applications may be produced by a variety of electrical discharge devices [5-8]. For some industrial and domestic applications, pulsed discharges are much more suited because of their high selectivity, capability of removing various pollutants simultaneously, moderate operating conditions, and relatively low maintenance requirements resulting in relatively low energy costs of the pollutant treatment. However, ANTP technology for indoor air treatment has the disadvantage to produce undesirable by-products [9-11]. To overcome the by-products formation and increasing energy efficiency, ANTP could take advantage of its synergetic effect through combination with heterogeneous catalysts [12].

In this work, various catalysts were combined with a DBD for VOCs abatement at room temperature. Reported results concern the effect of the catalyst, the plasma and the plasma-catalyst on the conversion efficiency of toluene used as a representative VOCs. A systematic investigation is carried out in order to select the optimal positioning of the catalyst regarding the plasma discharge.

2. Experimental

2.1. Plasma reactor

The plasma reactor that we used is a DBD reactor in a cylindrical configuration. A schematic view of DBD reactor is shown in figure 1. That configuration gives the possibility to combine heterogeneous catalyst with plasma reactor in two different ways: by introducing the catalyst in the discharge zone (*in-plasma catalysis*, IPC configuration) or by placing the catalyst downstream the discharge zone (*post-plasma catalysis*, PPC configuration). The plasma reactor was powered by a high voltage AC generator delivering HV amplitude up to 18 kV at a frequency of 50 Hz.

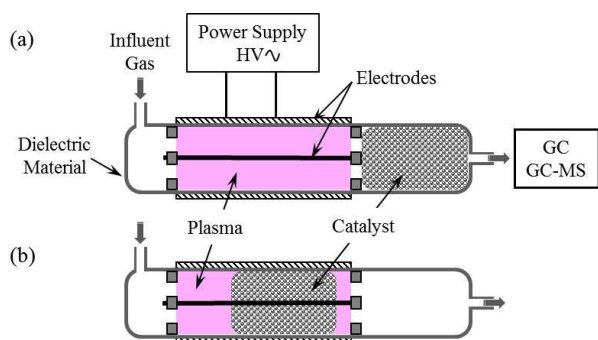


Figure 1: Schematic overview of the two plasma-catalyst hybrid configurations: (a) PPC and (b) IPC.

2.2. Catalyst materials

Catalysts in powder form includes: OMS-2, 5 - 15wt% CuO/OMS-2, 5 - 10wt% Co₂O₃/OMS-2, CeO₂, 1 wt% Au/CeO₂, 5 - 15wt% Co₂O₃/Al₂O₃, Al₂O₃, 1 - 2 wt% Ag/Al₂O₃, 1 wt% Au/Al₂O₃, LaMnO₃, LaMnO₃/Al₂O₃, La_{0.7}Ag_{0.3}MnO₃, La_{0.7}Ag_{0.3}MnO₃/Al₂O₃, and Nb₂O₅.

The supported metal catalysts were prepared by the wetness impregnation method. The aqueous solutions of nitrate salts ((Cu(NO₃)₂·3H₂O, Co(NO₃)₂·6H₂O, AgNO₃,) were slowly heated at 70°C until all the precursor was completely dissolved. A calculated amount of the support (OMS-2, Al₂O₃) was added to the solution. The

slurry was heated to approximately 80-100°C and stirred until the total evaporation of water. The samples thus obtained were dried at 120°C and then, calcined at 500°C in air for 4 hours.

Au/support catalysts and OMS-2 catalysts have been prepared by the method described in [13, 14]. Perovskite catalysts (LaMnO₃, La_{0.7}Ag_{0.3}MnO₃) were prepared by the citrate method. All the catalysts have been characterized by XRD, IR-Spectroscopy, and FE-SEM.

Measurements of the activities of catalysts were performed in a continuous flow fixed-bed reactor. The total flow rate through the catalyst bed was kept constant at 4 L/h (O₂: 0.8 L/h, N₂: 3.2 L/h) leading a weight hourly space velocity (WHSV) of 20 000 h⁻¹). Toluene concentration was fixed at 800 ppm. Under standard reaction conditions, the gas mixture was fed over 200 mg catalysts introduced in the plasma reactor in *post-plasma* or *in-plasma* configuration.

Reactants and reaction products were analyzed by GC (HP 6890 Series II) equipped with electron capture detector (ECD), and Phenomenex ZB5 column (30 m x 0.25 mm, i.d. of 0.25 μm) and GC-MS (Agilent Technologies 5973) equipped with flame ionization detector (FID) and HP5 column (30 m x 0.18 mm, i.d. of 0.32 μm).

3. Results

Systematic experiments of toluene conversion were carried out in three systems: (i) only heterogeneous catalysts, (ii) only ANTP, and (iii) ANTP-catalyst hybrid system in two combinations (IPC and PPC).

3.1. Catalytic removal of toluene

The catalytic activity is expressed in terms of:

- T_e: End temperature reaction corresponding i.e. temperature required for 95% conversion.
- T_i: Ignition temperature reaction i.e. temperature for the beginning of the catalytic reaction.

Figure 2 shows the data giving T_i and T_e for toluene conversion as a function of the nature of catalyst. The reaction of toluene conversion over perovskite, Al₂O₃, and OMS-2 based catalysts are promoted at high temperature. As example, these data indicates that T_i and T_e are in the range of 300-480°C in the case of Al₂O₃, and 200-400°C

when OMS-2 was used. In the presence of catalyst modified with Cu, Co, Ag, or Au, the ignition temperature decreases drastically to reach 90°C in the case of 1wt% Au/Al₂O₃.

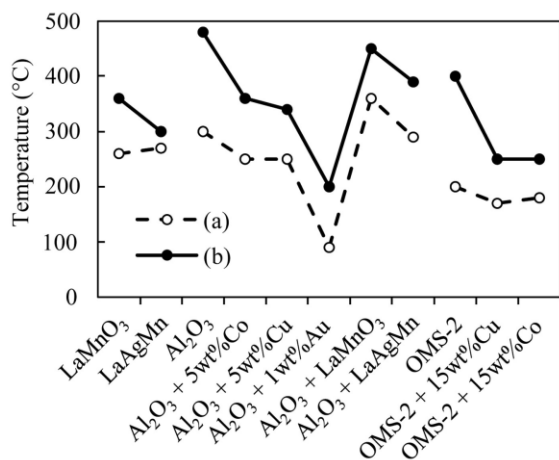


Figure 2: Toluene oxidation temperatures: Ignition reaction (a) and end reaction (b) as a function of the nature of catalysts.

The supported metals on OMS-2 need a high loading (10 - 15wt%) of Cu or Co to reach a high activity. In comparison to OMS-2 alone, T_e over 15wt%Cu/OMS-2 decreases from 400°C to 250°C. Obviously, adding Co, Ag, or Cu creates new active sites which change the activity of the catalysts. Similar behavior was observed in the case of perovskite catalyst.

3.2. Plasma removal of toluene

In the absence of catalysts, the plasma plays a role of "oxidative media". A significant fraction of input plasma energy is dissipated in the dissociation of O₂ which becomes the dominant process because O₂ dissociation is much more efficient than N₂ dissociation in the electron energy range produced. This dominant oxidation process leads to the formation of the main products of the plasma such as O₃, CO, CO₂, and NO_x (NO+NO₂). In our experimental conditions, toluene conversions in the range 55-60% were obtained. As expected, the plasma partially oxidizes the toluene leading to the formation of by-products such as formic acid (HCOOH), acetic acid (CH₃COOH), and benzene (C₆H₆).

3.3. Plasma-catalytic removal of toluene

Systematic experiments were carried out for the two catalyst positions in regard to plasma reactor. When the IPC is operated, short lifetime reactive species, in the range of tens of nanoseconds, as radicals and excited states (O(³P), O(¹D), OH, ...) created by the ANTP can be used efficiently by the

catalyst. On the contrary, when the catalyst is placed post-plasma (PPC), long lifetime reactive species, in the range of milliseconds, such as O₃, H₂O₂, NO, and NO₂ could be used.

The ANTP-catalyst hybrid system is operated at room temperature. The toluene removal efficiency significantly increases when the catalyst was coupled to the plasma reactor whatever the nature of catalyst used. The toluene conversion measured over 0 - 15wt%Cu/OMS-2 catalysts is reported Figure 3. By increasing the loading of Cu from 0 to 15 wt%, the toluene conversion increases from 70 to 79% for IPC and from 65 to 69% for PPC. Similar results were obtained when Co was substituted to Cu at the same contents.

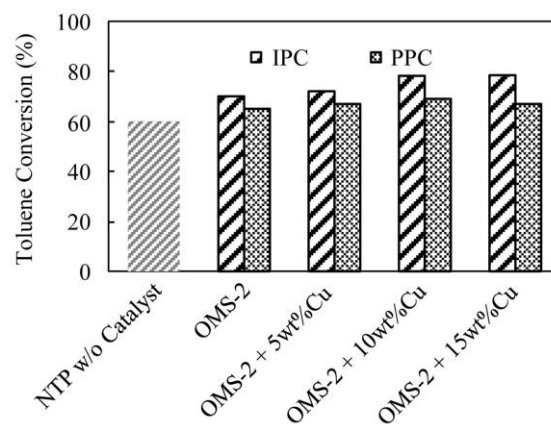


Figure 3: Toluene conversion over Cu/ OMS-2 catalysts

Figure 4 shows toluene conversions over alumina based catalysts. Results clearly show that the highest toluene conversion (up to 96%) was obtained when 1wt% Au/Al₂O₃ was used into the plasma discharge. However, when these catalysts were positioned in the post-discharge region, lower toluene removal (up to 80%) was measured. One can notice that, in the absence of catalyst, the toluene removal efficiency was only 60%.

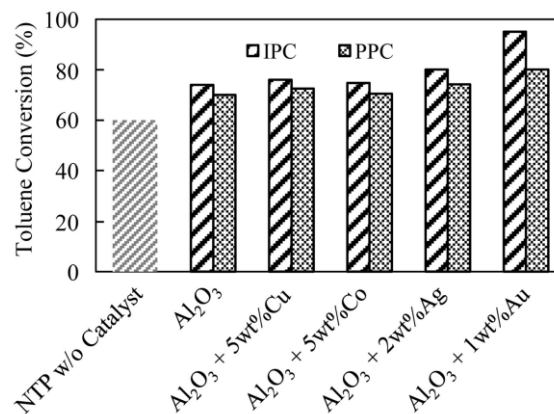
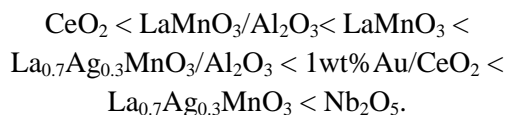


Figure 4: Toluene conversion over metal/ γ -Al₂O₃ catalysts

Table 1 summarizes the activity of CeO₂, Nb₂O₅ and perovskite catalysts. As shown in previous data, the IPC configuration seems to be better suited for toluene conversion. In that configuration, the conversion of toluene over various catalysts follows the order:



Catalyst	Toluene Conversion (%)	
	PPC	IPC
CeO ₂	62	75
1wt%Au/CeO ₂	80	90
LaMnO ₃	70	85
LaMnO ₃ /Al ₂ O ₃	65	78
La _{0.7} Ag _{0.3} MnO ₃	73	92
La _{0.7} Ag _{0.3} MnO ₃ /Al ₂ O ₃	71	88
Nb ₂ O ₅	89	96

Table 1: Toluene conversion over CeO₂ and Al₂O₃ based catalysts, Nb₂O₅, and perovskite.

The products of toluene oxidation measured at the outlet of the plasma-catalyst system are CO₂, CO, and H₂O. In contrast to plasma experiments without catalyst, ozone and NO_x are not measured as reaction products. It means that the toluene reaction conversion occurs at room temperature by consumption of O₃ and NO_x produced by the plasma discharge. Deposit accumulation was observed on the wall of the plasma reactor. This deposit was identified as benzyl alcohol, benzoic acid, and 5-Methyl-2-Nitrophenol.

4. Conclusion

Atmospheric dielectric barrier discharge was combined to various catalysts in two configurations (*in-plasma* (IPC) and *post-plasma* (PPC) *catalysis*) for the abatement of toluene at room temperature.

Without plasma, the reaction of toluene conversion over different catalysts (perovskite, Al₂O₃, and OMS-2 based catalysts) is promoted at high temperature (higher than 200°C, depending on the nature of the catalyst).

In the absence of catalyst, the toluene removal conversions were in the 55- 60% range and the reactions products were O₃, CO, CO₂, and NO_x.

When the plasma was combined to catalyst, the toluene removal efficiencies strongly increased

when the catalysts were in IPC position. Best toluene removal conversions, up to 96%, were obtained when using 1wt% Au/Al₂O₃ and Nb₂O₅ catalysts. The products of the toluene oxidation were CO and CO₂.

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