



Acetone and ethanol vapor oxidation via negative atmospheric corona discharge over titania-based catalysts



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ABSTRACT

The paper is devoted to the oxidation of acetone and ethanol vapors by means of an optimized negative atmospheric corona discharge combined with TiO₂-based catalysts located in a post-plasma position. A series of studied samples includes CuO-MnO₂/TiO₂, CuO/TiO₂ and MnO₂/TiO₂ with 3 wt% of copper oxide and 6.8 wt% of manganese oxide. Experiments were performed at room temperature in a closed 404-L chamber with a ~0.9-L active plasma region. It was shown that the use of the catalysts can provide a significant reduction in the concentrations of ozone and oxidation byproducts and a three-fold increased conversion of the reactants. It was unexpectedly found that copper oxide, as an active agent, did not significantly change the effect of post-plasma-located TiO₂. The manganese-containing sample was found to be the best catalyst at the conditions considered. The presence of this catalyst in the post-plasma position inhibits the formation of unwanted products (O₃ and CO) and promotes the deep oxidation of acetone and ethanol with increased selectivity toward CO₂.

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1. Introduction

Population of the planet is faced with the global problem of environmental pollution. Various industrial and agricultural processes are the common source of air pollution, and their existence is a problem for human health and the environment in general. A great part of pollutants are Volatile Organic Compounds (VOCs). This category includes most solvent thinners, degreasers, cleaners, some lubricants, and liquid fuels [1]. Some VOCs are dangerous to human health and harm the environment. A number of control technologies are used to alleviate the pollution problem. They are basically divided into two groups: destruction and recovery methods. Recovery is a relatively good method for a wide range of purification tasks. However, its main drawback is the need for the regeneration of sorbent materials. In contrast, destruction-based methods do not have this disadvantage because pollutants are transformed into mostly harmless inorganic compounds.

One promising destruction-based method has recently gained a lot of attention. It is the oxidation of VOCs by means of a combination of an atmospheric Non-Thermal Plasma discharge (NTP oxidation) with catalysts. Generation of NTP in air is a well-known

method of air purification [2,3], which is characterized by relatively low capital and operational costs. However, it has drawbacks such as poor energy efficiency and generation of ozone and other harmful by-products, which decreases the selectivity of oxidation of VOCs toward CO₂. A combination of the NTP with catalysis may possibly reduce the negative effects of the NTP and improve the performance of purification systems.

There are a number of reviews on the treatment of VOCs using a combined plasma-catalytic oxidation [4–7]. The combination of plasma with catalysts was found to be reasonable because plasma produces many active species like electrons, ions, free radicals, excited species, and photons, and all of them can participate directly or indirectly in oxidative reactions over a catalyst. Combined plasma-catalytic systems can be divided into single-stage systems, also called In-Plasma Catalysis (IPC) or Plasma-Driven Catalysis (PDC), and two-stage systems, also called Post-Plasma Catalysis (PPC) or Plasma-Enhanced Catalysis (PEC). Systems of both types have their own advantages and limitations. The IPC provides a combination of simultaneous gas-phase and surface reactions. A catalyst located inside the plasma region can also affect the discharge. Porous catalytic materials placed into an IPC system may enhance selectivity toward the formation of CO₂ [8]. However, IPC systems are difficult to optimize. Besides, because of technical limitations, they are based mostly on the Dielectric Barrier Discharge (DBD) [9], which is very difficult to scale. In contrast, PPC systems are more capable of optimization because both the

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discharge and the catalyst can be varied independently. In the PPC oxidation, plasma promotes a partial conversion of pollutants and a generation of ozone and other active species, which can enhance the oxidation to CO_2 over a post-plasma catalyst.

A variety of catalytic materials can be used for the PPC at room or elevated temperatures. For example, the oxidation of ethanol and acetone with ozone has been performed at 300–573 K over manganese oxide supported on alumina or on silica [10,11]. It was shown that ethanol reacted with O_3 at a lower temperature than with O_2 , and with a lower activation energy. The oxidation of acetone with ozone was also highly accelerated on both catalysts. The only detected carbon-containing product was CO_2 . Another example of the PPC is the use of a commercial ozone decomposition catalyst ($\text{CuO} + \text{MnO}_2$)/ TiO_2 for toluene removal. It was shown that the application of this catalyst improved the removal efficiency up to 40 times [12]. In addition, the destruction of ozone over a MnO_2 catalyst was found to enhance the destruction of benzene vapors [13].

In our earlier research, we investigated the oxidation of acetone and ethanol vapors in an atmospheric pressure corona discharge (CD) at a near room temperature [14,15]. For generating the NTP, we used a double-wire-to-plane discharge gap geometry and found the optimal wire diameter, polarity and power input that provided the highest cost efficiency. However, we have also faced such well-known problems of air purification with the CD as relatively low energy efficiency and the formation of oxidation by-products and ozone.

The present paper demonstrates our results of placing catalysts $\text{CuO-MnO}_2/\text{TiO}_2$, CuO/TiO_2 , and $\text{MnO}_2/\text{TiO}_2$ downstream the CD unit, i.e., in the post-plasma position. Such a combination of the NTP and catalysis can help to reduce the drawbacks of plasma application and improve the total efficiency of the system. The samples were compared to determine the optimal composition of a post-plasma catalyst for the purpose of air purification. A large free-air volume (i.e., the volume not exposed to plasma) is the main distinction of our experimental setup. In our opinion, this approach is closer to the conditions of the practical application of air purification techniques.

2. Experimental

2.1. Chemicals

High purity acetone, 96% ethanol, and room air at atmospheric pressure with relative humidity about 45–50% were used in the experiments without preliminary cleaning.

2.2. Experimental setup

The used experimental setup is very similar to that described in detail previously [14,15]. A scheme of the experimental setup is demonstrated in Fig. 1A. A stack of double-wire-to-plane discharge units was placed inside a 404-L Plexiglas chamber connected to an FTIR analysis system. The most efficient regime of the CD was selected on the basis of our previous results [15]: the diameter of corona wire was 0.8 mm, the corona current was fixed at 1 mA, and the corresponding voltage across the discharge gap was about 13 kV, which corresponds to the discharge power of 13 W.

To create a PPC system, a mesh support with a deposited catalyst (Fig. 1B) was located in the post-plasma position (downstream the corona discharge unit at the distance 350 mm). The air flow rate was $135 \text{ m}^3/\text{h}$ in presence of catalytic support. The mass of the catalyst was about 2.5 g. The support with the size of $13.5 \text{ cm} \times 14.5 \text{ cm}$ was made of fiberglass mesh impregnated with aqueous $\alpha\text{-Al}_2\text{O}_3$ and an inorganic binder based on $\gamma\text{-Al}_2\text{O}_3$.

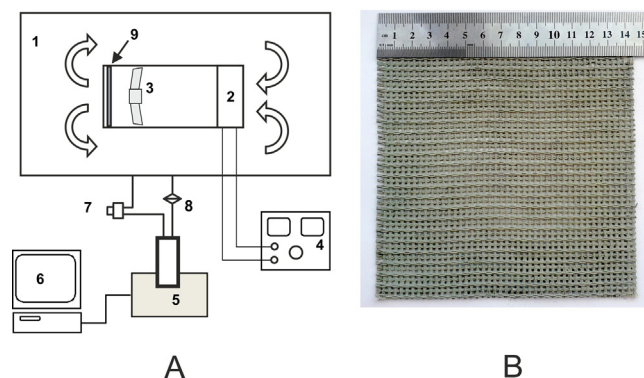


Fig. 1. (A) Scheme of the experimental setup: (1) test chamber (404 L), (2) corona discharge unit, (3) fan, (4) high voltage DC power supply source, (5) FTIR spectrophotometer Vector 22 (Bruker) with multipass gas cell, (6) computer, (7) membrane pump, (8) $0.2 \mu\text{m}$ filter, (9) fiberglass mesh with deposited catalyst; (B) photo of the fiberglass mesh with deposited $\text{MnO}_2/\text{TiO}_2$ sample.

In every experiment, the initial vapor–air mixture contained 200 ppm of a studied substrate. The mixture was purged through the cell using plastic tubing and a $0.2\text{-}\mu\text{m}$ air filter under the action of a membrane pump. Concentrations of organic vapors, O_3 , CO , and CO_2 in the chamber were measured with an FTIR spectrophotometer Vector 22 (Bruker) equipped with a multipass gas cell of 0.7 L volume. The FTIR spectrophotometer allowed continuous measuring of concentrations of reagents and products. The FTIR spectra were recorded in the wavenumber range $450\text{--}4000 \text{ cm}^{-1}$ with the resolution of 1 cm^{-1} at 30 s intervals. Each spectrum represents an average of 10 scans. Concentrations of organics and CO_2 were calculated from the areas of absorption bands in the IR spectra. The rates of changes in substance concentrations were calculated by using a linear approximation. Original software Difference was used for the processing of numerous spectra. Calculations were based on a novel method of spectral subtraction of gas-phase FTIR spectra by minimizing the spectrum length [16].

2.3. Catalyst preparation

TiO_2 Hombifine N ($S_{\text{BET}} = 350 \text{ m}^2/\text{g}$) was used as a basis for preparing the catalysts. The deposition was performed by the impregnation method. Copper and manganese nitrates ($\text{Cu}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$) were used as precursors for copper and manganese oxides. TiO_2 was impregnated with a 0.5-M aqueous solution of precursors. Then, the mixture was dried at 120°C and calcined at 500°C for 5 h. The aqueous solution was deposited on the mesh after cooling and grinding the catalyst.

The list of synthesized catalysts with the targeted oxide content (by weight) is shown in Table 1. The series of samples includes pure TiO_2 Hombifine N and five samples of TiO_2 modified with CuO and/or MnO_2 . The whole set of samples allows one to reveal a number of correlations and to elucidate the role of an added oxide. Sample 1 is a reference sample. Samples 2 and 3 would show the effect of each additive separately. Samples 4–6 would give information about the dependence of sample properties on the order of additive deposition. Additional experiments without any catalyst were carried out for both acetone and ethanol to make a comparison with an ordinary NTP oxidation.

The catalysts were characterized by X-Ray Diffraction analysis (XRD), X-Ray Photoelectron Spectroscopy (XPS), and Transmission Electron Microscopy (TEM). The XRD analysis of the samples was carried out with a Bruker D8 Advance with the copper irradiation (wavelength 1.5418 \AA). The XPS analysis of some samples (3, 5, 6 and sample 5 after use) was performed using a SPECS apparatus. The spectrometer was equipped with a semispherical analyzer

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