

Toluene oxidation by non-thermal plasma combined with palladium catalysts

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The oxidation of toluene in air was investigated using a dielectric barrier discharge (DBD) combined with Pd/Al₂O₃ catalysts. When using only plasma, rather low selectivity towards CO₂ was obtained: 32-35%. By filling the DBD reactor with Pd/Al₂O₃ catalyst the CO₂ selectivity was significantly enhanced (80-90%), however, a large amount of toluene was desorbed from the catalyst when the discharge was operated. By filling a quarter of the discharge gap with catalyst and placing the rest of the catalyst downstream of the plasma reactor, an important increase of CO₂ selectivity (~75%) and a 15% increase in toluene conversion were achieved as compared to the results with plasma alone.

The emission of volatile organic compounds (VOC) from various industrial processes represents a significant source of air pollution, and therefore VOC removal from waste gas with high efficiency and low costs is an issue of major importance for human health and the environment. Plasmas are highly efficient in producing radicals and oxidizing species, which react to the VOC molecules and decompose them. However, plasma activation is rather non-selective, therefore, in order to obtain simultaneously high conversion and high selectivity towards total oxidation, the addition of catalysts appears promising [1-3]. Noble metal catalysts (Pd, Pt, Au, Ag) were tested in many works, due to their high efficiency for VOCs abatement [4-6].

In this work the total oxidation of toluene in air by plasma-assisted catalysis was investigated at room temperature and atmospheric pressure. The experiments were carried out in dry air, since it is known that humidity has negative effect on VOCs decomposition in plasma-catalytic systems [6]. Non-thermal plasma was generated in a dielectric barrier discharge in coaxial geometry. The plasma reactor consisted in a quartz tube with the inner diameter of 9 mm. The inner electrode was a metallic rod of 3 mm diameter placed on the axis of the reactor. The outer electrode was aluminum tape placed on the outside of the tube on a length of 48 mm.

The discharge was operated in ac mode, with sinusoidal voltage, at 50 Hz frequency. The amplitude of the applied voltage was varied in the range 10-20 kV and the corresponding values of the average power were 0.16-0.88 W. The experimental data were scaled to the specific input energy (SIE), defined as the ratio of the power and flow rate. For the gas flow rate used in this work (163 mL/min) the SIE was in the range 59-324 J/l.

Palladium catalysts supported on γ -Al₂O₃ were used in the experiments. The catalysts were prepared by impregnating γ -Al₂O₃ with an acid solution of PdCl₂ then dried after a program of temperatures at 110 °C, ashed at 500 °C for 2 h and reduced in hydrogen flow at 400 °C for 4 h. Palladium concentration in the catalysts was 2%.

The conversion of toluene in plasma, in the absence of the catalysts, was ~8% for the lowest input energy used and reached 48% for highest SIE. The main gaseous reaction products of toluene oxidation in the plasma were carbon dioxide and carbon monoxide. The selectivity to CO₂ showed a slight increase with SIE and was in the range 32-35%. Fig. 1 shows the selectivity to CO₂ as a function of SIE obtained with plasma alone and with the plasma-catalytic system.

In a first set of experiments 2.24 g catalyst were introduced in the DBD reactor, occupying the entire discharge gap. Initially, the gas was passed through the reactor for several hours with plasma off, so that toluene was adsorbed on the catalyst bed until saturation was reached. After the plasma was turned on, a large amount of toluene was desorbed from the catalyst. Although an important part of the toluene was converted mainly to CO₂ (selectivity 80-90%, see Fig. 1), the effluent gas still contained a high concentration of toluene, therefore this configuration was not effective for toluene removal.

In the following experiments only 0.56 g of catalyst were placed in the discharge region. In this case the toluene conversion was similar with that obtained with plasma alone, but the concentration of carbon oxides (CO + CO₂) in the effluent gas increased significantly (with 40-70%) as compared to

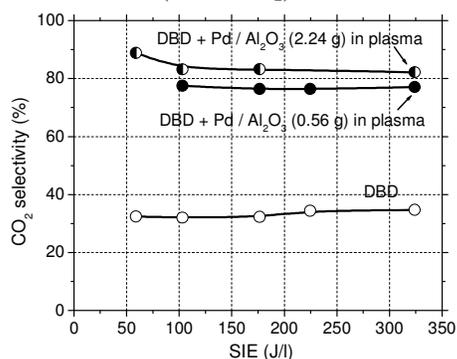


Fig. 1: CO₂ selectivity as a function of SIE in the plasma and in the plasma-catalytic system

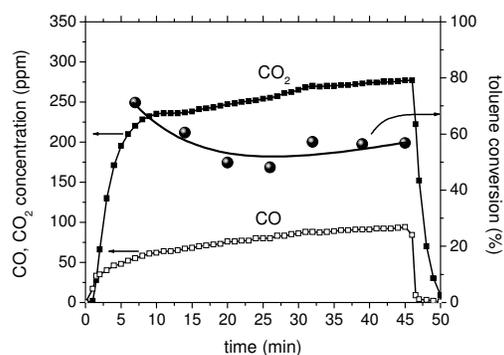


Fig. 2: Temporal evolution of CO and CO₂ concentrations and toluene conversion

the results obtained with plasma alone, due to conversion of adsorbed toluene. The selectivity to CO₂ was 76-77% regardless of SIE. Clearly, the presence of Pd/Al₂O₃ catalysts significantly improved the process selectivity towards total oxidation.

Another experiment was performed with 0.56 g catalyst placed inside the discharge area and 1.7 g catalyst placed downstream of the plasma reactor. This experiment was carried out for an amplitude of the applied voltage of 17 kV, corresponding to a SIE of 225 J/L. The temporal evolution of toluene conversion and CO₂ and CO concentrations is shown in Fig. 2. The conversion showed an initial decrease of about 15% and then became stable around 56%, which represents an improvement as compared to the result obtained with plasma alone: 41% at the same SIE. The CO₂ selectivity showed also a slight decrease in time, from 80% to 75%, but is still largely enhanced as compared to 35% in plasma.

A further advantage of using this configuration is the complete removal of ozone in the effluent gas. In plasma, in the absence of catalysts, the O₃ concentration increased with increasing SIE in the range 0.4-1.18 g/m³. The O₃ concentration was reduced to 0.02-0.12 g/m³ with 2.24 g of catalyst introduced in the plasma zone and was completely removed when the catalyst was placed in post-plasma configuration.

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