TOLUENE OXIDATION IN A DIELECTRIC BARRIER DISCHARGE COMBINED WITH HETEROGENEOUS CATALYSIS*

M. MAGUREANU[1], D. PIROI[1], N.B. MANDACHE[1], V.I. PARVULESCU[2]

[1]National Institute for Lasers, Plasma and Radiation Physics, Atomistilor Str. 409, 077125 Magurele, Romania, E-mail: daniela.piroi@infim.ro, E-mail: monimag@infim.ro, E-mail: mandache@infim.ro
[2]Department of Chemical Technology and Catalysis, Faculty of Chemistry, University of Bucharest, Bd. Regina Elisabeta 4-12, 030016 Bucharest, Romania, E-mail: v_parvulescu@yahoo.com

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The oxidation of toluene in contaminated air streams was investigated using non-thermal plasma, both in the absence and in the presence of several Ag/Al_2O_3 catalysts, placed downstream of the plasma reactor. The catalysts did not significantly influence toluene conversion, but improved the process selectivity towards total oxidation.

Key words: non-thermal plasma, dielectric barrier discharge, plasma-catalysis, toluene.

1. INTRODUCTION

The emission of volatile organic compounds (VOC) from various industrial processes represents a major source of air pollution [1, 2]. Therefore, VOC removal from waste gas with high efficiency and low costs is an issue of major importance for human health and the environment in general. Total oxidation of the VOC is desired, with formation of CO_2 and H_2O. Conventional thermal and catalytic oxidation are useful at high VOC concentration, however, they become inefficient at low concentrations [1, 2]. Non-thermal plasma (NTP) offers great potential for the initiation of chemical reactions in the gas phase: the high-energy electrons generated in the plasma react with gas molecules producing chemically active species and thus a highly reactive environment is created without spending energy for heating the entire gas [1-4]. However, plasma activation is rather non-selective and in order to obtain simultaneously high conversion and high selectivity towards total oxidation, the combination of plasma and catalysis appears promising [3-7].

In this work toluene was chosen as a model VOC. Toluene is an aromatic hydrocarbon that is widely used as an industrial feedstock and as a solvent. Inhalation of toluene vapors negatively affects human health and can cause severe

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neurological harm. The total oxidation of toluene in air was investigated using a dielectric barrier discharge (DBD), both in the absence and in the presence of Ag/Al_2O_3 catalysts, placed downstream of the plasma reactor.

2. EXPERIMENTAL SET-UP

Toluene vapor was introduced by passing a flow of air through a vessel containing liquid toluene. The concentration was adjusted by adding a flow of ambient air, and adjusting both flow rates by mass flow controllers. The total gas flow rate was 510 sccm and the initial concentration of toluene in air was 50 ppmv.

The discharge was generated in a DBD reactor with coaxial geometry, packed with spherical quartz pellets of 2 mm diameter. A description of the plasma reactor is also available in [8]. The plasma reactor consisted in a quartz tube with the outer and inner diameters of 22 mm and 19 mm, respectively. The inner electrode was a metallic rod of 11 mm diameter placed on the axis of the reactor. The outer electrode was a silver layer on the outside of the tube on a length of 10 cm.

The electrical circuit is described in detail and its schematic drawing is given in [9]. Briefly, a high voltage transformer (transformation ratio 300) provides sinusoidal voltage at 50 Hz frequency. The high voltage was applied to the inner electrode and the outer electrode was grounded. The discharge voltage was measured by a high voltage probe (Tektronix P6015). The current was determined from the voltage drop across a shunt resistor (3 Ω) connected in series with the grounded electrode. The total charge was measured with a non-inductive capacitor (1 μF), placed instead of the shunt resistor. The voltage, charge and current were monitored by a digital oscilloscope (Tektronix TDS 2022). The electrical power dissipated in the discharge was calculated by the Lissajous method [10].

The effluent gas was analyzed by gas chromatography (GC-2014, Shimadzu, FID detector). The concentrations of CO_2 and CO resulting from toluene oxidation were monitored continuously by a gas analyzer (Ultramat 6, Siemens) coupled on-line.

Three Ag/Al_2O_3 catalysts were investigated, denoted AlAg13, AlAg23 (Ag content 3%) and AlAg25 (Ag content 5%). The catalysts were prepared following a recently reported procedure [11]. Silver colloids prepared by reducing $AgNO_3$ in aqueous solution with sodium citrate were embedded in alumina, which was formed *via* a surfactant assisted synthesis. Aluminum butoxide ($Al(OBu)_3$ - 98.5 g) was dissolved in isobutanol (150 cm^3) and was subsequently added to an isobutanol (90 cm^3) solution of 17.2 g Pluronic 84 ($((EO)_{19}(PO)_{39}(EO)_{19})$) which acted as the surfactant. The resulting mixture was then heated to 70 ^oC for 6 h. Water was added, and the reaction was maintained at 80 ^oC for 10 h followed by 100 ^oC for 20 h. The Ag colloid dissolved in water was added to this mixture under vigorous stirring. The samples were preserved at room temperature for 48 h, dried under vacuum at 110 ^oC, and then calcined at 500 ^oC with a slope of 0.5 $^oC\ min^{-1}$. The

Ag content was confirmed by ICP-AES analysis. Using this methodology the following samples resulted: AlAg13, containing 3 wt.% Ag, when the molar ratio alkoxide:alcohol:water was of 1:10:25, AlAg23 and AlAg25, containing 3 and 5 wt.% Ag, respectively, when the molar ratio alkoxide: alcohol:water was of 1:5:10.

The catalysts (100 mg) were placed in a catalytic reactor situated downstream of the plasma reactor. The catalysts were heated up to 100 ^{o}C.

3. RESULTS AND DISCUSSION

The plasma experiments were performed for applied voltage amplitudes of 11.5, 17 and 23 kV. The corresponding values of the discharge power were 0.66 W, 1.75 W and 2.92 W, respectively and the specific input energy (SIE), defined as the ratio of the power and flow rate was 77, 209 and 360 J/l, respectively.

The conversion of toluene in the plasma, in the absence of catalyst, increased with increasing SIE: it was around 17% for the lowest input energy used and reached 60% for highest one. The main gaseous reaction products detected from the decomposition of toluene in plasma were carbon monoxide and carbon dioxide. No significant effect of the input energy on the products selectivity was observed. The selectivity to CO_2 was 37-39% over the SIE range investigated.

The catalysts were analyzed by various techniques [11]. ICP-AES analysis was used to determine the Ag content. Textural characterization was performed ex-situ by BET nitrogen physisorption at −196 ^{o}C. Surface area and pore size values were calculated from nitrogen adsorption–desorption isotherms recorded on a Micromeritics ASAP-2010 automated instrument. All the catalysts are characterized by high surface area: the AlAg13 catalyst has a surface area of 400 m^2/g, AlAg23 – 330 m^2/g and AlAg25 – 333 m^2/g.

X-ray diffraction was performed using a Shimadzu XRD-7000 with Cu Kα (λ = 1.5418 Å, 40 kV, 40 mA) radiation at a scanning rate of 0.10 min^{-1} in the 2θ range of 10–80^{o}. The XRD patterns exhibit broad lines assigned to amorphous γ-Al_2O_3 phase and lines due to metallic Ag particles [11]. ^{27}Al MAS-NMR spectra showed a line located at around 13 ppm, corresponding to hexacoordinated aluminum and a second line at 74-76 ppm generally assigned to tetracoordinated aluminum. The increase in Ag loading leads to a shift of the line assigned to tetracoordinated aluminum towards higher values, which might be related to slight distortion of tetracoordinated aluminum sites due to Ag incorporation [11]. XPS analysis (Specs GmbH) showed the preservation of the Ag(0) state even after calcinations. TEM analysis (JEOL JEM-1010 instrument, 100 kV) confirmed the preservation of the size of the colloids and the mesoporous texture. The amorphous alumina showed a fiber-like texture and silver particles of 3-5 mm were observed. The texture is better organized in AlAg13 as compared with the other catalytic materials, and therefore 13-AgAl has larger pore volume and uniform pore size, which agrees well with BET data [11].

The catalytic experiments, in the absence of the plasma, as well as the plasma-catalytic experiments were carried out for catalyst temperatures of 80°C and 100°C. At these low temperatures the catalysts alone did not decompose toluene.

In the plasma-catalytic system it was found that the addition of the catalysts did not influence significantly toluene conversion. However, the selectivity to CO_2 was improved in the presence of catalysts as compared to the values obtained by plasma alone. Fig. 1 shows the selectivity to CO_2 in the plasma and in the plasma-catalytic system as a function of SIE, for the three catalysts investigated heated to 100 °C.

The best results were obtained for the AlAg 13 catalyst, while the other two catalysts gave 5-10% lower selectivity to CO_2. The highest value for the CO_2 selectivity was 65% as compared to 37% with plasma alone, for SIE of 77 J/l. With increasing SIE the CO_2 selectivity shows a decrease. However, this is compensated by the much higher conversion at high SIE. The yield (defined as the amount of toluene converted to CO_2) is about 3 times higher at 350 J/l SIE as compared to the one obtained at 77 J/l.

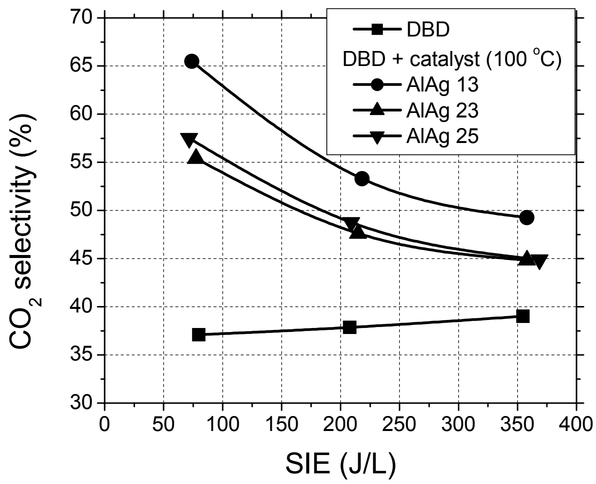

Fig. 1 – Selectivity to CO_2 as a function of SIE in the plasma and in the plasma-catalytic system for the three catalysts investigated heated at 100°C.

Fig. 2 shows the selectivity to CO_2 as a function of SIE in the plasma and in the presence of AlAg 13 catalyst, for temperatures of 25 °C, 80 °C and 100 °C.

It was found that even at room temperature the selectivity to CO_2 was greatly enhanced as compared to that obtained by plasma alone. For the same value of SIE, the selectivity to CO_2 increased with increasing catalyst temperature.

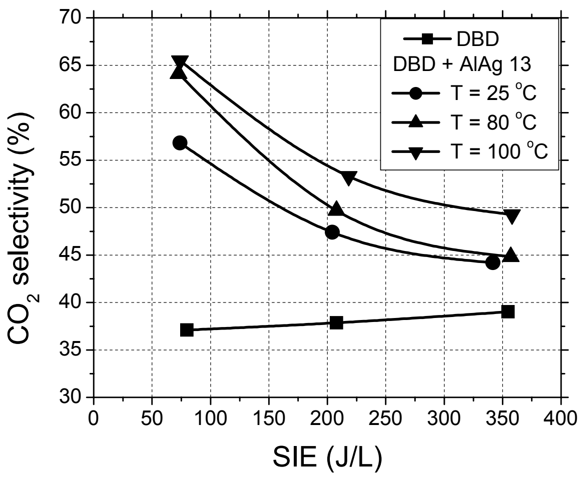

Fig. 2 – Selectivity to CO_2 as a function of SIE in the plasma and in the presence of AlAg 13 catalyst, for the three temperatures investigated

Toluene decomposition by plasma-catalysis was investigated in [6] using also Ag/Al_2O_3 catalysts placed inside a $BaTiO_3$ packed-bed reactor. The authors reported toluene conversions below 10% for plasma SIE of 60 J/l and catalyst temperatures below 200 ^oC, a significant increase of conversion occurring only above 300 ^oC. The study focused solely on the temperature effect on toluene decomposition and no data concerning products selectivity were reported.

The lower selectivity towards CO_2 obtained in the plasma-catalytic system at higher SIE might be due to catalyst poisoning by one of compounds present in the effluent gas: unreacted toluene, ozone, nitrogen oxides, carbon oxides. Unreacted toluene can be ruled out, since its concentration is higher at lower SIE and decreases with increasing SIE. The concentration of ozone in the effluent gas varied in the range 0.6-1.2 g/m^3 over the SIE range investigated. It was not the object of the present study to quantify the nitrogen oxides formed in the plasma, however their presence in the effluent gas was detected in small amounts in other works [12, 13] and therefore it is expected also in the present experiments. The role of ozone in the oxidation of hydrocarbons and CO was investigated in [14] using a combination of non-thermal plasma and γ-Al_2O_3. The authors found that the catalytic function of γ-Al_2O_3 was deactivated in time. However, the deactivation of γ-Al_2O_3 did not occur in the absence of hydrocarbons, indicating that the characteristic products of a discharge in air (*e.g.* NOx, OH and O radicals, O_3) do not cause a measurable deactivation of the catalyst [14]. Ag/Al_2O_3 catalysts prepared by the same procedure as in the present work have been tested for catalytic removal of NO in the presence of hydrocarbons (propene and decane) under real exhaust gas conditions [11]. Catalysts analysis after the reaction showed that neither the oxidation state of the nanoparticles, nor the relative surface concentration of metal changed by exposure of the catalysts to the reaction conditions [11]. Roland *et al.* [14] concluded that CO_2 resulting from the total oxidation of hydrocarbons is responsible for poisoning the catalytic sites of γ-Al_2O_3. This might be a reason for the lower selectivity towards total oxidation observed in the present experiments at high SIE. More detailed investigations regarding this aspect are under study.

4. SUMMARY

Toluene was decomposed in a plasma-catalytic system consisting in a DBD reactor and Ag/Al_2O_3 catalysts placed downstream and heated up to 100 ^{o}C. In the plasma, in the absence of catalyst, toluene conversion varied in the range 17-60% for SIE in the range 77-360 J/l. The main gaseous reaction products detected were CO and CO_2. The SIE does not influence significantly products selectivity; the selectivity to CO_2 was 37-39%. In catalytic experiments, in the absence of the plasma, toluene was not decomposed at temperatures below 100 ^{o}C.

In the plasma-catalytic system it was found that the addition of the catalysts did not influence significantly toluene conversion. However, the selectivity to CO_2 was improved in the presence of catalysts, reaching values up to 65%, as compared to the values obtained by plasma alone. The data obtained clearly suggest a synergetic effect between the plasma and the catalysts. This effect is mainly due to catalytic oxidation with ozone produced in the DBD, since the catalysts are not active at such low temperature.

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