Removal of dilute trichloroethylene in air by post-plasma catalysis over Cu-Mn mixed oxides

Zhiping Ye,[a,b] Jean-Marc Giraudon,[a] Savita K P Veerapandian,[b] Nathalie De Geyter,[b] Rino Morent,[b] Jean-François Lamonier[a,*]

[a]*Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, Lille, 59000, France*

[b]*Ghent University, Faculty of Engineering, Department of Applied Physics, Research Unit Plasma Technology, Sint-Pietersnieuwstraat 41, Ghent, 9000, Belgium*

**Corresponding author: jean-francois.lamonier@univ-lille1.fr*

Abstract: This study investigates the removal of dilute trichloroethylene (TCE) in moist air by post-plasma catalysis (PPC) using Cu-Mn mixed oxides heated at 150°C and located downstream of the plasma reactor (non-thermal plasma = NTP). In comparison to the catalytic oxidation and non-thermal plasma process, PPC was found to be the best process to convert TCE into CO_2, in particular when Cu-Mn oxide was synthetized by redox precipitation method. Cu-Mn oxide prepared by co-precipitation method showed a lower TCE conversion but a better stability in the PPC process for TCE abatement.

Keywords: Volatile Organic Compounds, Post-Plasma Catalysis, Cu-Mn mixed oxides.

1. Introduction

The combination of NTP and a catalyst for trichloroethylene (TCE) removal has attracted increasing interest because this process can significantly outperform the plasma alone and thermal catalysis experiments in terms of efficiency, selectivity and energy cost[1]. If the catalyst is located after the discharge zone (post-plasma catalysis (PPC)), the preprocessing of TCE by plasma treatment assists the sequential catalytic oxidation by lowering TCE concentration and forming ozone. Catalytic reactions can take advantage of the NTP emitted O_3 as a potential source of active oxygen species enabling further oxidation of both TCE and potential NTP gaseous hazardous by-products. Hence, the selection of catalysts for TCE abatement in a PPC process should consider some important criteria, such as ozone decomposition ability, TCE total oxidation capacity, as well as hydrothermal stability and resistance to chlorine. Copper-manganese mixed oxides have demonstrated their great ability for ozone decomposition[2], CO oxidation[3] and chlorinated VOCs removal[4], and their resistance to the deactivation caused by chlorinated byproducts[5]. Therefore TCE removal was studied using copper manganese oxides, synthetized using two different methods, heated at 150°C and positioned in the downstream of the plasma. Textural and surface characterizations of fresh and used catalysts were performed in order to make some correlations between their physico-chemical properties and their performances in the TCE abatement.

2. Experimental

The TCE abatement by PPC was investigated in moist air ([TCE] = 300 ppm ; RH=15%) using a 10-pin-to-plate negative DC corona discharge and Cu-Mn mixed oxides as catalysts. For better comparison the TCE abatement was also investigated with plasma alone at room temperature during 1 hour (Energy Density (ED) : 60 ; 90 ; 120 J/L) and catalyst alone from 100 to 300°C (2°C/min) with analysis every 50°C. The performance of each configuration was evaluated in terms of total TCE conversion, CO_2 and CO_x yields and byproducts distribution. The copper manganese oxides were prepared either by a co-precipitation method (sample $CuMn_2O_4$-P4) using metal nitrates as precursors, tetramethylammonium hydroxide (TMAH) as precipitant or by a redox-precipitation method (sample $CuMnO_x$-R3) using manganese acetate and copper nitrate as precursors, permanganate of potassium as oxidant. The fresh and used materials have been characterized by ICP-OES, N_2 physisorption, XRD and XPS analyses.

3. Results and discussion

During the NTP experiments a poor mineralization of TCE into CO_x was observed since the highest yield obtained was 13% for the energy density of 120 J/L. This low CO_x yield in NTP experiments can be explained by the formation of polychlorinated organic by-products. In the TCE catalytic oxidation, it was shown that both catalysts ($CuMnO_x$-R3 and $CuMn_2O_4$-P4) are very active and selective to CO_2 in the temperature range 200-300°C. In comparison with some reference catalysts used in the total oxidation of TCE, $CuMnO_x$-R3 and $CuMn_2O_4$-P4 exhibited very good catalytic activity (T_{50} = 250°C). Figure 1 shows the TCE conversion into CO_2 as a function of energy density (60-120 J/L) for the two catalysts in PPC configuration in comparison with the NTP alone and catalyst alone configurations. The TCE conversion into CO_2 is significantly improved in PPC configuration when compared to NTP and in particular using $CuMnO_x$-R3 catalyst. The superior catalytic performance of CuMnOx-R3 can be explained by its high specific surface area and high redox properties. However the activity of CuMnOx-R3 for the TCE degradation slightly decreased during the 1h of testing at 150°C, evidencing the deactivation of this catalyst during the analysis. This deactivation can be related to the accumulation of chlorine at the surface (Figure 2).

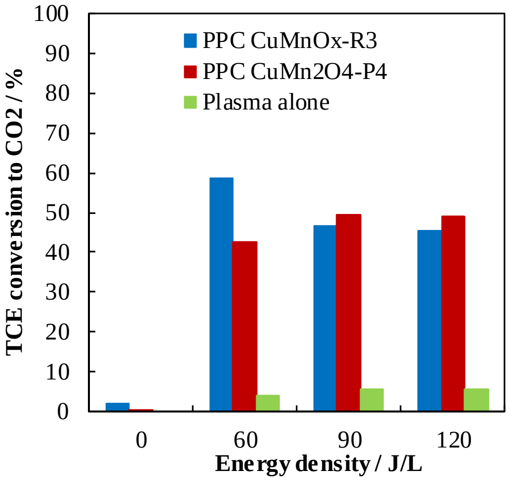

Figure 1. TCE conversion into CO_2 for catalysis, NTP and PPC experiments.

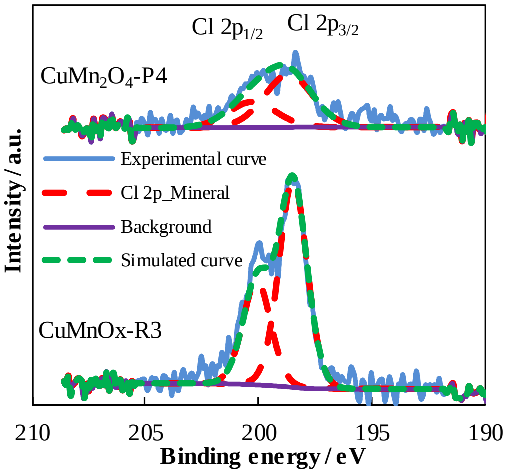

Figure 2. Cl 2p XPS spectra of catalysts after PPC experiments.

When comparing to MnO_x and CeMnOx tested in the same pin-to-plate DC corona plasma reactor, except that the number of pins herein is increased from 5 to 10,[6] $CuMnO_x$-R3 and $CuMn_2O_4$-P4 exhibits better performance in terms of TCE conversion into CO_2. The comparison of the ozone amount in the outlet gas stream after TCE abatement as a function of ED in NTP and PPC configurations allows to conclude to ozone decomposition over the catalyst surface as crucial factor. The improvement of CO_2 yield could be related to the facile oxidation of polychlorinated by-products by active oxygen species coming from the O_3 decomposition.

4. Conclusions

PPC process was found to be the best process to convert TCE into CO_2 with catalyst temperature of 150°C. A remarkable increase of CO_2 yield has been observed due to the facile oxidation of polychlorinated by-products at the surface of Cu-Mn mixed oxides which are suitable materials for ozone decomposition.

References

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