

Effects of preparation conditions and crystal phase of manganese-loaded γ - Al_2O_3 catalyst on the plasma-catalytic removal of o-xylene

Lian Wang¹, Hong He^{1*}, Changbin Zhang¹, Yafei Wang¹

¹ Research Center of Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China

*corresponding author: honghe@rcees.ac.cn

Introduction

Volatile organic compounds (VOCs) such as benzene, toluene, and xylene (BTX) are harmful to the environment and human health. Therefore, the removal of VOCs for purification of indoor air and gaseous industrial streams is an important research topic. Catalytic oxidation techniques are effective and environmentally friendly ways to eliminate VOCs such as formaldehyde, thoroughly converting them into CO_2 and H_2O [1]. However, up to now, catalytic oxidation techniques have not been able to effectively remove BTX at room temperature [2]. Non-thermal plasma (NTP) generated by an electrical discharge is effective for the removal of VOCs due to the generation of strong oxidizing agents like ozone, hydroxyl radical, atomic oxygen, etc. However, the use of the NTP technique in VOCs abatement has some disadvantages, such as high energy consumption and generation of unwanted by-products. The combination of NTP and catalysis has the potential to overcome the limitations of non-thermal plasma or catalytic oxidation alone, and has been extensively studied [3-6]. In this work, we report our recent development in the removal of o-xylene in air by the combined use of non-thermal plasma and a $\text{Mn}/\text{Al}_2\text{O}_3$ catalyst placed after the discharge zone. The effects of $\text{Mn}/\text{Al}_2\text{O}_3$ preparation conditions, including use of different precursors, loading amounts, and calcination temperatures, and crystal phase present (α -, β -, γ -, or δ - MnO_2) on the conversion of o-xylene, selectivity of CO_2 , carbon yield, and discharge byproduct formation were systematically investigated.

Materials and Methods

A dielectric barrier discharge (DBD) plasma system with a 100 mm length DBD zone was constructed with a high-frequency AC high voltage power supply source, and catalysts were introduced after the discharge zone in air (1000 mL/min, 300 ppm o-xylene). The o-xylene concentration was analyzed online by a GC-MS. CO_2 and CO concentrations were analyzed by a GC equipped with FID detector. O_3 and NO_x concentrations were determined by O_3 and NO_x detectors. Other oxidation products were detected by online FT-IR. The α -, β -, γ - and δ - MnO_2 nanorods were synthesized by a hydrothermal method according to the literature [7]. $\text{Mn}/\text{Al}_2\text{O}_3$ catalysts were prepared through impregnation or ball-milling methods.

Results and Discussion

Compared with plasma alone, $\text{Mn}/\text{Al}_2\text{O}_3$ addition was found to efficiently improve the o-xylene conversion with low specific energy density and suppress formation of undesirable byproducts such as O_3 and NO_x (Figure 1). The $\text{Mn}/\text{Al}_2\text{O}_3$ catalyst prepared with manganese acetate precursor showed the highest catalytic activity, with 80% conversion of o-xylene at a specific energy density as low as 100 J/L. Manganese acetate precursor, 6 wt% Mn loading amount, 400 and 500 °C calcination temperatures, and α - $\text{MnO}_2/\text{Al}_2\text{O}_3$ were the optimum conditions for preparation of catalysts with excellent catalytic activity for o-xylene removal.

The ($\text{CO}+\text{CO}_2$) yield was greatly increased by the α - $\text{MnO}_2/\text{Al}_2\text{O}_3$ catalyst and was two-fold higher than that obtained using 6 wt% $\text{Mn}/\text{Al}_2\text{O}_3$. Furthermore, other byproducts such as CH_3CHO and $\text{HCOOH}/\text{CH}_3\text{COOH}$ were also found. XRD and XPS results indicate that the presence of microcrystalline MnO_2 , greater amounts of Mn^{4+} species and enrichment of lattice oxygen on the surface of the catalyst improved the catalytic activity in the oxidation of o-xylene.

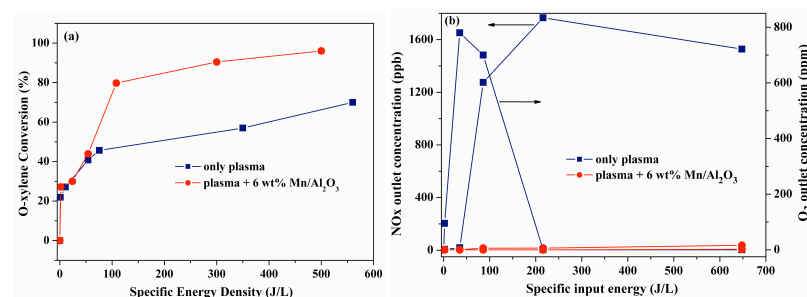


Figure 1. Effects of catalyst on the (a) o-xylene conversion and (b) NO_x and O_3 formation, 6 wt% $\text{Mn}/\text{Al}_2\text{O}_3$ was prepared with manganese acetate precursor.

Significance

It was found that manganese acetate precursor, 6 wt% Mn loading amount, 400 and 500 °C calcination temperatures, and α - $\text{MnO}_2/\text{Al}_2\text{O}_3$ were the optimum conditions for preparation of catalysts for plasma-catalytic removal of o-xylene. Microcrystalline MnO_2 , greater amounts of Mn^{4+} species and enrichment of lattice oxygen on the surface of the catalyst were responsible for higher catalytic activity in the oxidation of o-xylene.

References

1. Zhang, C. B.; He, H.; Tanaka, K. I. *Catalysis Communications* **2005**, *6*, 211.
2. Li, W. B.; Wang, J. X.; Gong, H. *Catalysis Today* **2009**, *148*, 81.
3. Ogata, A.; Yamanouchi, K.; Mizuno, K.; Kushiya, S.; Yamamoto, T. *Plasma Chemistry and Plasma Processing* **1999**, *19*, 383-394.
4. Subrahmanyam, Ch.; Renken, A.; Kiwi-Minsker, L. *Chemical Engineering Journal* **2010**, *160*, 677.
5. Guo, Y. F.; Ye, D. Q.; Chen, K. F.; He, J. C.; Chen, W. L. *Journal of Molecular Catalysis A: Chemical* **2006**, *245*, 93.
6. Fan, X.; Zhu, T. L.; Wang, M. Y.; Li, X. M. *Chemosphere* **2009**, *75*, 1301.
7. Liang, S. H.; Teng, F.; Bulgan, G.; Zong, R. L.; Zhu, Y. F. *Journal of Physical Chemistry C* **2008**, *112*, 5307.