Plasma induced toluene decomposition on alumina-supported Mn-based composite oxides catalysts

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Plasma induced toluene decomposition on alumina-supported Mn-based composite oxides catalysts

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Abstract. This paper presents a two-stage hybrid plasma catalyst system for toluene decomposition in air. It consists of a dielectric barrier discharge reactor and Mn-based composite oxides catalysts. Experimental results show that removal efficiency of toluene was 10 % by only plasma, but a 100 % destruction efficiency as well as 100% ozone removal was achieved by plasma catalysis at a specific energy density of 28.8 J L^{-1}. The catalytic decomposition efficiency of toluene and ozone produced in the first stage is in the following order: NTP+ Mn-Co/Al > NTP + Mn-Ce/Al > NTP+ Mn-Ni/Al > NTP. Compared to other catalysts coupled with non-thermal plasma in a two-stage plasma catalytic reactor, the alumina-supported Mn-based composite oxides catalysts showed a better performance for toluene and ozone removals, especially the Mn-Co/Al catalyst.

1. Introduction

Air pollution with volatile organic compounds (VOCs) has been one of the serious environmental problems because of its toxicity, destruction of the ozone layer and through photochemical smog. As an alternative to low concentration VOCs abatement techniques, non-thermal plasma has been widely investigated for its unique properties such as moderate operating conditions and high-energy electrons with short residence times[1-3]. The energetic electrons excite, dissociate and ionize the gas molecules producing chemically active species such as O and OH radicals, which will result in VOC conversion to CO_2, H_2O and other products [4]. However, plasma alone has many disadvantages such as the plasma energy consumption, CO_2 selectivity, and toxic by-products [5, 6]. A new attempt to overcome these limitations is the combination of the NTP method with catalysis. The hybrid reactor can be a single-stage (SPC) or a two-stage (TPC) system. For many cases, a better performance could simply be achieved by a catalytic post-treatment of the NTP effluent in a two-stage system. The main role of the catalyst bed is to recycle O radicals via the slipped O_3 [7-9]. Alumina-supported transition metals have been widely investigated based on the high reactivity for ozone decomposition [10, 11].

In this work, various catalytic materials based on Mn supported on Al_2O_3 were combined with a dielectric barrier discharge (DBD) for toluene abatement at room temperature. Detailed comparison experiments of toluene decomposition are performed in order to evaluate any synergistic effects between the plasma and the catalyst.

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2. Experimental system

2.1. Plasma/catalyst system

The reaction system is as reported previously [12]. The non-thermal plasma is produced by using a dielectric barrier discharge (DBD) reactor. A stainless steel high-voltage electrode is placed inside a silica tube with a copper mesh grounded electrode. The active length and the discharge gap are 10 cm and 2 mm, respectively. A 50 Hz AC high-voltage power source is used for energizing the reactor. All experiments are performed under atmospheric pressure and room temperature.

Toluene is flushed out from a tubular saturated at zero centigrade degree with dry air under a flow rate of 6.0 mL min^{-1}. After mixing with air, the total gas flow rate is 500 mL min^{-1} for present work, which corresponds to the gas hourly space velocity (GHSV) of the catalysis bed of 150,000 h^{-1}, and initial toluene concentration of 107 parts per million (ppm). Gaseous analyses are carried out with an on-line gas chromatograph (Fuli GC-9750) and iodometric titration.

2.2. Materials

Various catalytic materials based on Mn supported on Al2O3 in powder form have been tested to select the highest active catalyst. The Co-Mn/Al, Ce-Mn/Al and Ni-Mn/Al catalysts were all prepared by the deposition precipitation method, and Co-Mn, Ce-Mn, Ni-Mn mol ratio were 1:1. The catalysts' BET surface areas are 181.53, 183.23 and 166.02 m2 g-1, respectively.

3. Results and discussion

3.1. Effect of catalysts on toluene conversion and ozone decomposition

Figure 1 shows the conversion of toluene using Mn-Co/Al catalysts of different Mn-Co loading amounts. At SIE of 19.9 J L^{-1}, an increase in the Co-Mn amount increases the decomposition efficiency of toluene. For example, toluene conversion of 10wt% Co-Mn loading amount is 70%. When increasing the loading amount to 30 wt%, toluene conversion increases to 88%. On the other hand, when SIE>28 J L^{-1}, toluene can be almost removed irrespective of the Mn-Co loading amounts. This means that a good synergistic effect between the plasma and the Mn-Co/Al catalyst can also be achieved with a low metal loading amount.

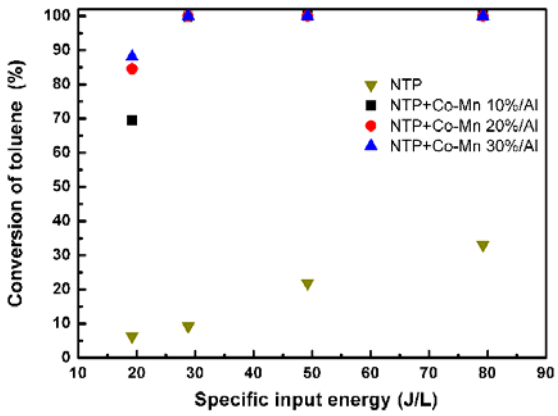

Figure 1. Effect of Mn-Co loading amount on the conversion of toluene.

Figure 2 and figure 3 show conversion of toluene via the SIE and residual ozone concentration using γ-Al_2O_3 catalysts supported with Co-Mn, Ce-Mn and Ni-Mn. Hereafter, the catalysts with 30 wt% are used for the catalytic tests. For both toluene and ozone decomposition, the catalyst reactivity is in the order of Co-Mn/Al ＞Ce-Mn/Al > Ni-Mn/Al. For example, at the SIE value of 28.8 J L^{-1}, the plasma reactor induced decomposition rate is about 10%, but increases to 100 % by integrating the

Co-Mn/Al catalyst. At the same time, 100% of ozone is destroyed. Ozone is the only oxidant in the post-plasma which can be utilised to oxidise toluene via its decomposition to produce oxygen atom [13]. These findings indicate that the γ-Al_2O_3 plays an important role in the decomposition of both toluene and ozone. This might be due to the larger BET specific surface area with Al_2O_3 supported.

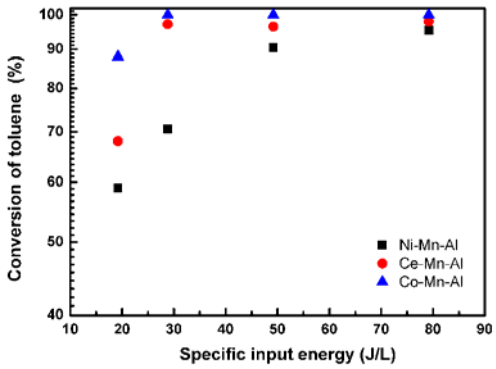

Figure 3. Conversion of toluene via the SIE over using γ-Al_2O_3 supported with Co-Mn, Ce-Mn and Ni-Mn catalysts.

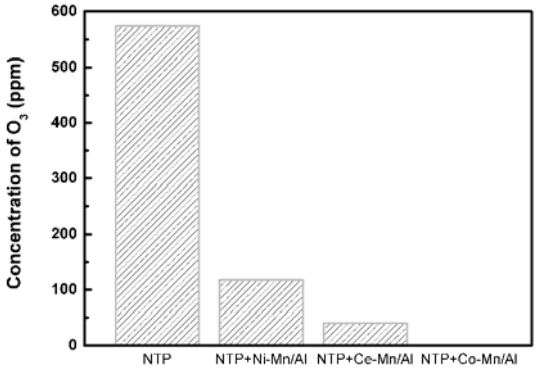

Figure 4. Residual ozone concentration using γ-Al_2O_3 catalysts supported with Co-Mn, Ce-Mn and Ni-Mn.

4. Conclusions

Based on present experimental investigations, we can give the following remarks:

(1) The alumina-supported Mn-based composite oxides catalyst is found to be very effective for the post-plasma system due to its larger specific surface area.

(2) The Mn-Co/Al catalyst possesses both high activity toward toluene removal and ozone decomposition. Toluene can be almost removed at SIE of 28.8 J L^{-1} with no ozone residue.

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