Catalytic ozonation of gaseous benzene over MnOx/ZSM-5 at ambient temperature: prevention of catalyst deactivation and byproducts emission

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Introduction
Catalytic oxidation of VOCs is highly desirable at ambient temperature due to its environmental-friendliness and energy-saving. In recent, catalytic oxidation by using ozone (catalytic ozonation) has attracted much attention for complete oxidation of VOCs at low concentration levels under mild conditions. However, there are still some challenges related to this method for practical application. One of the biggest challenges is the deactivation of catalysts. Besides of organic intermediates, residual ozone and CO from incomplete benzene oxidation are also toxic inorganic compounds. The inhibition of byproducts presents another big challenge. These issues must be solved before its practical application of catalytic ozonation.

In this study, highly active MnOx/ZSM-5 catalysts with good stability were developed by impregnation method and used to catalytic ozonation of benzene, a model VOC, at ambient temperature.

Materials and Methods
A series of ZSM-5 zeolite (Si/Al=200) supported transition metal oxide catalysts (Mn, Co, Cu, Fe, Ni, Zn and Ce) were prepared by impregnation method using acetate as precursor. The experiments were run in a fixed bed continuous-flow reactor. They were conducted at a GHSV = 48,000 h⁻¹ and 25 °C. If not specifically indicated, the inlet benzene, ozone concentration and relative humidity (RH) is 30 ppm, 450 ppm and 50%, respectively. The concentrations of benzene, CO and CO₂ formed from benzene oxidation were monitored by GC online.

Results and Discussion
Figure 1 shows time course for catalytic performance over various ZSM-5 supported metal oxide catalysts. The metal oxide catalysts exhibited great difference in catalytic ozonation of benzene. Benzene removal efficiency followed the order: Mn > Co > Cu > Ni > Zn > Ce > Fe. Among them, Fe and Ce catalysts showed the poorest activity. They tended to gradually deactivated after reaction of about 100 min and completely lost activities soon. Mn exhibited the highest catalytic activities for benzene oxidation. Benzene removal efficiency kept at 100% for about 320 min.

Figure 2 shows time course for removal efficiency of benzene and decomposition rate of ozone in dry and wet flow over Mn/ZSM-5 catalyst. The Mn catalysts deactivated in wet flow was quickly regenerated as water vapor is cut off: Benzene removal efficiency and ozone decomposition rate was increased to 100% and 80%, respectively in dry flow and kept stable after even a long run (800 min). Once water vapor was fed, they quickly lost catalytic activity again. Benzene removal efficiency and ozone decomposition rate was quickly decreased. Water vapor seriously poisoned Mn/ZSM-5 catalyst and significantly reduced catalytic activity. It should be mainly responsible for catalyst deactivation. This is probably due to that the adsorbed water occupied the active sites of Mn, which prevented the reaction of benzene and ozone. Compared with CO₂ selectivity of 84.7% in wet flow, it was increased to nearly 100% in dry flow (not shown).

Figure 1. Time course for benzene oxidation with various catalysts

Figure 2. Time course for removal efficiency of benzene and decomposition rate of ozone in dry and wet flow over Mn/ZSM-5 catalyst

Significance
Mn/ZSM-5 exhibited the best performance among the prepared metal oxide catalysts during catalytic ozonation of benzene. The catalyst deactivation and byproduct emission can be greatly inhibited by lowering the relative humidity or improving reaction temperature. At reaction temperature of 50 °C or in dry flow, both benzene removal efficiency and CO₂ selectivity was kept at nearly 100%. Ozone can be completely also eliminated at 50 °C.

References