

THE CATALYTIC DEGRADATION OF PCDD/Fs IN GAS PHASE WITH MESOPOROUS $\text{Cu}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ SPINEL OXIDES

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Introduction

Catalytic destruction is now emerging as a new viable alternative for the safe treatment of organohalogenated compounds¹. Several studies have indicated that noble metals and transition metal oxides have the higher ability to catalyze the degradation of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) in the laboratory scale experiments. However, it may be not appropriate to adopt them to large-scale applications due to their high cost and rapid deactivation². Therefore, some efforts have been made to develop metal oxide composite catalysts with low cost for the catalytic degradation of organohalogenated compounds^{3,4,5}.

Spinel-type complex oxides are represented by the chemical formula AB_2O_4 , in which A ions are generally divalent cations occupying tetrahedral sites and B ions are trivalent cations in octahedral sites. The metal oxide composites with spinel structure cost much lower, and the preparation technology is simple. Many researches have adopted these composites as catalysts for the safe treatment of organohalogenated compounds in solution or solid matrix^{6,7,8,9}. To our knowledge, no research has concerned about the degradation of PCDD/Fs in the gaseous phase under the catalysis of spinel-type complex oxides. In the present work, the mesoporous $\text{Cu}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ spinel oxides was prepared, and its catalytic effect for the degradation of PCDD/Fs in the gaseous phase was explored. The volatile PCDD/Fs were generated from the thermal desorption treatment of municipal solid waste incineration (MSWI) fly ash. The objectives of this study are to develop a technology for reducing the gas-phase emission of PCDD/Fs from the thermal desorption treatment of MSWI fly ash.

Materials and Methods

The spinel-type $\text{Cu}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ catalyst were prepared by a co-precipitation method as described elsewhere^{10,11}. The ash sample was taken from a MSWI plant in Guangdong province of China. The ash was vibrated and homogenized. Experimental device are shown in Figure 1. Nitrogen gas was used as the carrier to flow through a desorption pipe with full of MSWI fly ash at a fixed velocity of 24 ml/min. The temperature of the desorption pipe was under control by a calorifier. Thermal desorption of the PCDD/Fs from MSWI fly ash was conducted for 1 h. Carrier gas containing PCDD/Fs was passed through the second reaction column (20 mm long \times 4 mm i.d.) with catalysts and the temperature was under control too. The tail gas was passed through an adsorbent U tube with *n*-hexane in ice bath boiler, by which most of volatile PCDD/Fs was captured. Finally, the residue PCDD/Fs in the gas phase was collected by XAD-2 resin.

When the catalytic degradation reaction was finished, the tube wall of gas path tube was washed by *n*-hexane, and the catalysts and the XAD-2 resin were mixed as one solid sample. Soxhlet extraction was conducted for solid sample using 250 ml of toluene for about 24 h. The extraction and the washing solution *n*-hexane were mixed as one sample. The concentrations of PCDD/Fs were accurately quantified by an Autospec Ultima high resolution mass spectrometer (Micromass, UK) interfaced with a Hewlett-Packard (Palo Alto, CA, USA) 6890 Plus gas chromatograph (HRGC/HRMS). The details about sample preparation and instrumental analysis were described in our previous paper¹².

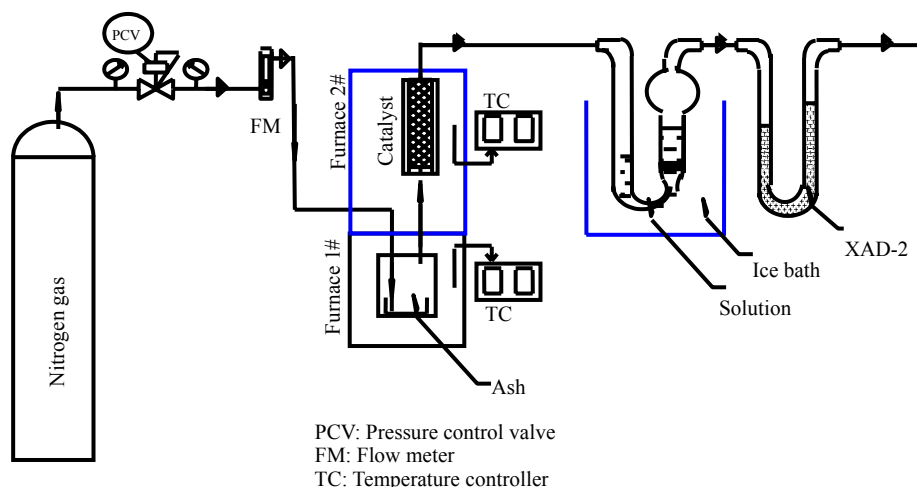


Figure 1. Schematic diagram of catalytic degradation apparatus.

Results and Discussion

Thermal desorption of PCDD/Fs from MSWI fly ash

Thermal desorption treatment of MSWI fly ash were carried at 250 °C, 300 °C, 350 °C and 400 °C, respectively. The total concentrations of tetra- to octa-CDD/Fs in the thermally-treated fly ash and gaseous phase with different temperatures were shown in Figure 2. At 250–350 °C, above 93% of tetra- to octa-CDD/Fs was desorbed, and the desorption ratio of higher chlorinated dioxin congeners was significantly lower than those with less chlorine atoms. The sum of tetra- to octa-CDD/Fs concentrations in gas phase and thermally-treated fly ash at 250–350 °C were obviously lower than those in the original MSWI fly ashes. However, when the temperature reached at 400 °C, The Sum of tetra- to octa-CDD/Fs concentrations in gas phase and thermally-treated fly ash were obviously increased relative to the original MSWI fly ash. This result indicated that PCDD/Fs can be formed significantly at 400 °C.

Catalytic degradation of PCDD/Fs in gas phase

Figure 3 and Figure 4 show the degradation efficiency of the total concentration and total I-TEQ for PCDD/Fs as a function of reaction temperature for the $\text{Cu}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ spinel-type catalysts. Under the nitrogen atmosphere, the removal efficiency of PCDD/Fs by the catalysis of $\text{Cu}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ spinel-type catalysts was obviously better than that by CuO. The catalytic degradation efficiency of PCDD/Fs within three catalysts was in the order: $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4 > \text{Cu}_{0.5}\text{Mg}_{0.5}\text{Al}_2\text{O}_4 > \text{CuO}$. The result was uniform with the research of the dechlorination degradation of HCB over $\text{Cu}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ spinel oxides¹¹. The reaction efficiency of catalytic degradation of PCDD/Fs on these two spinel oxides were both above 80%, indicating that the spinel oxide has the higher ability to degrade dioxins in gaseous phase. The degradation efficiency of PCDD/Fs on $\text{Cu}_{0.5}\text{Mg}_{0.5}\text{Al}_2\text{O}_4$ showed an increasing trend first and then decreased with the rising of temperature, indicating that the temperature was an important parameter for the catalytic degradation with $\text{Cu}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ spinel-type catalysts.

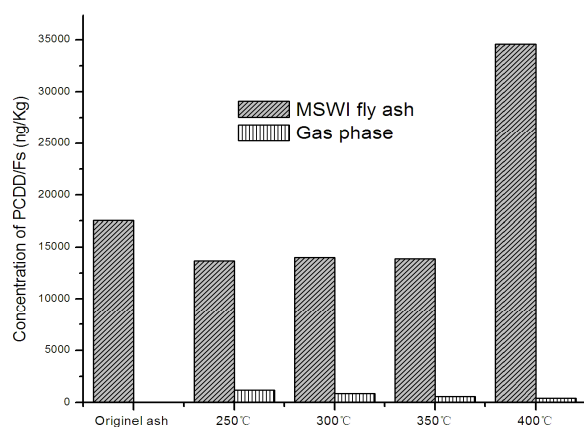


Figure 2 Concentrations of tetra- to octa-CDD/Fs in the thermally-treated MSWI fly ashes and gaseous phase at different temperatures.

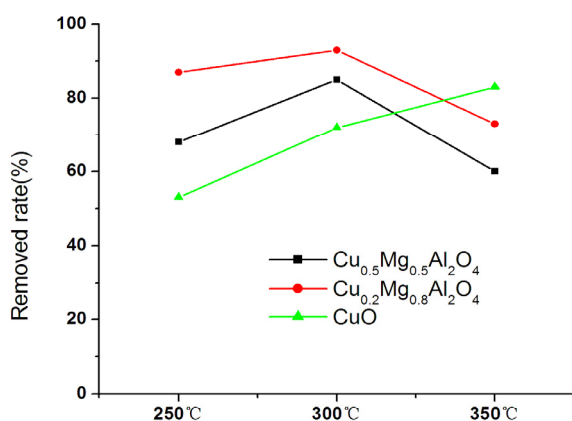


Figure 3 Removal rates of the total tetra- to octa-CDD/Fs

In this experiment, the removal rates of total concentration of tetra- to octa-CDD/Fs were overall higher than those of the I-TEQ value. This result suggested that a part of higher chlorinated components was hydrogenated and dechlorinated to the lower chlorinated components with the larger toxic equivalent. From the analysis of the concentration for each dioxin component, the removal rates of high chlorinated components, OCDD, HpCDDs, OCDF and HpCDFs, were all above 99.9% at 350 °C, which almost achieve completely degradation. However, the removal rates of lower chlorinated components such as TCDDs and TCDFs were significantly decreased contrast. The removal rate of TCDFs only was 48% at 350 °C. The removal rates of total I-TEQ for dioxins by the catalytic degradation with $\text{Cu}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ spinel-type catalysts at 350 °C were poorer than those at 250 °C and 300 °C. The present research of catalytic degradation for PCDD/Fs on spinel-like composite oxide will be continued. Improving the degradation efficiency, looking for the mild reaction conditions and exploring the mechanism of the catalytic process are the main directions for future research.

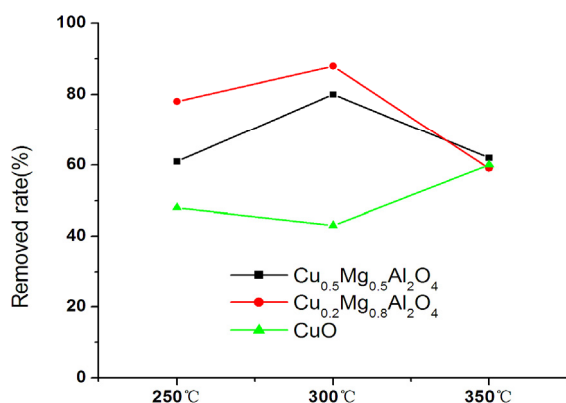


Figure 4 Removal rates of dioxins according to I-TEQ value.

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