EFFECT OF FLY ASH ON THE REMOVAL OF DIOXINS OVER SCR CATALYSTS

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Abstract
The effect of electrostatic precipitator (ESP) ash from the sinter plant on dioxin removal ability over a pelletized SCR catalyst based on $V_2O_5/WO_3/TiO_2$ was studied. Test measurements were taken at reaction temperatures of 250~320℃ and 2ng-TEQ/Nm^3 dioxin concentration at the inlet of the reactor. The ability to remove dioxins was shown to increase with the reaction temperature and the best performance occurred at 320℃, with an 83% conversion. The dioxin removal ability deteriorated substantially with the addition of ESP ash and the degree of deterioration resulting from the ESP ash addition became more prominent at the higher temperatures, with a 31% reduction at 320℃. The PCDDs (polychlorodibenzodioxins) were found to have better removal ability than the PCDFs (polychlorodibenzofurans) and the difference in the removal ability between the sparsely and the highly chlorinated PCDD/Fs species was reduced significantly as the amount of ESP ash or the operation temperature was increased. The change in the profile of the dioxin-like congeners was distorted by the de novo-synthesis induced by the ESP ash, which lowered the ability of the SCR catalyst to remove the dioxins.

Introduction
To meet the new dioxin emissions standard set by the Environmental Protection Agency (EPA) in Taiwan, the sinter plant in CSC has been urged to adopt a pipe-end dioxin reduction plan. At the outlet of sintering process, the flue gas is treated via a selective catalytic reduction (SCR) process and the dioxin concentration is reduced to 0.5ng-TEQ/Nm^3. Due to the high ESP ash concentrations contained in the flue gas, CSC uses plate-type catalysts for dioxin reduction. The SCR catalyst was originally solely intended for NOx removal. At present, the SCR catalyst has been redesigned to remove both dioxins and NOx at the same time.
In their study of the impact of ESP ash on the de novo-synthesis of dioxins, Xhrouet et al.[1] reported that the amount of PCDFs formed was about ten times than that of PCDDs, and that the major compositions of PCDFs predominated over the more sparsely chlorinated PCDFs species at temperatures of 325~400℃. Moreover, the ability to remove dioxins was shown to be more favorable with sparsely chlorinated PCDD/Fs species than with the more highly chlorinated PCDD/Fs species[2].
In this paper we report on a study of the effect of ESP ash on the removal ability of dioxins over a TiO_2-based SCR catalyst in order to test the relationship between the de novo-synthesis and the catalytic activity of the prepared SCR catalyst in the laboratory.

Materials and Methods
The prepared SCR catalyst was based on V_2O_5-WO_3-TiO_2 as the major components. The catalyst was prepared by kneading TiO_2 support with an aqueous mixed solution of ammonium vanadate (NH_4VO_3) and ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}$). The sample was dried and then calcined at 500℃ for 4 hrs. The catalyst was used in a pelletized form for the reaction tests.
The dioxin source was generated by extracting the fly ash obtained from the ESP of the sinter plant with n-hexane. The n-hexane solution was injected into the reaction system by a high precision micro pump and the n-hexane was decomposed at 500~550℃ before the dioxins were transported with air into the glass flow reactor. The generated dioxin concentration was around 2ng-TEQ/Nm^3. The dioxin removal reactions were tested in a glass flow reactor whose catalytic bed was 34mm in height and 12mm in diameter. The weights of 0.2g catalyst and 0.1~0.2g ESP ash were mixed with quartz sand in the reactor and the particle sizes of catalyst were around 1mm in diameter. The reaction temperature was maintained at 250~320℃, and the inlet total flow rate of the carrier gas, comprising 15%O_2 with N_2, was 320 mL/min. The gas hour space velocity (GHSV) of reaction flow was controlled at around 5000hr^{-1}.
The gas stream sampling was located at the outlet of the reactor. PCDD/Fs sampling, clean up and quantification were conducted in accordance with the USEPA Method 23A. Analysis of the 17 dioxin-like

congeners was performed with high resolution gas chromatography (HRGC)(HP6890 plus)/high resolution mass spectrometer (HRMS)(JEOL JMS-700) equipped with a fused silica capillary column DB-5 MS.

Results and Discussion

Structure Analysis The major components contained in SCR catalysts were analyzed and the results are shown as follows：the contents of Ti, V and W were 42wt%, 2.1wt% and 5.5wt %, respectively. The specific surface area of SCR catalyst after calcination was 68m^2/g.

Catalytic Activity An SCR catalyst was used to test the ability to remove the dioxin in this study. The catalytic activity of the prepared $V_2O_5/WO_3/TiO_2$ catalyst was tested within a temperature range of 250~320℃ with an inlet dioxin concentration of 2 ng-TEQ/Nm^3, and the results are shown in Fig.1. Figure 1 shows that the dioxin removal ability increased with the reaction temperature and that the highest removal ability was attained at around 83% when the temperature was measured at 320℃. This removability effect is consistent with the results reported in literature[3].

Comparing the dioxin removal abilities of the PCDDs and PCDFs, no obvious difference was observed between either set of congeners, as shown in Fig.2. The comparable ability for the removal of PCDDs and PCDFs was also reported by Liljelined et.al.[1] in a study with V_2O_5/TiO_2 as the catalyst.

From the test results of their dioxin removal abilities, selected PCDDs (7 species) and PCDFs (10 species) congeners were further investigated and the results for each species in both congeners are presented in Figures 3(A) and 3(B), respectively. Among the dioxin-like congeners, the sparsely chlorinated PCDD/Fs species (with 4~5 chlorine atoms) showed better removal ability than the highly chlorinated PCDD/Fs species (with 6~8 chlorine atoms). This degree of dechlorination is the common characteristic for the decomposition of chlorine-containing aromatic compounds, in which the removal ability decreases with the increase in the number of chlorine atoms.

In order to investigate the effect of ESP ash on the dioxin removal ability passing over the SCR catalyst, the ESP ash was added onto the catalytic bed. The tests were carried out under two different added weights of ESP ash: one test was with 0.1g ESP ash added to the catalyst; and the other was with the addition of 0.2g of ESP ash. The respective test results compared with those using the SCR catalyst alone are shown in Fig.1.

With the addition of 0.1g ESP ash, the dioxin removal ability increased with the reaction temperature, and the best performance occurred at 320℃ with a 73% conversion rate. Compared with the results of using an SCR catalyst alone, the mitigating effects of the ESP ash on dioxin removal ability was readily apparent, and the degrees of reduction were found to be 5% at 250℃, 9% at 280℃ and 12% at 320℃, respectively. On the contrary, the dioxin removal ability was shown to decrease with the reaction temperature as the weight of ESP ash was increased from 0.1g to 0.2g, and the best performance occurred at the lowest temperature of 250℃ with a 65% conversion rate. The degrees of reduction in the dioxin removal ability were further expanded with 10% at 250℃, 20% at 280℃, and 31% at 320℃, respectively. The largest reduction in the dioxin removal ability appeared at the highest temperature of 320℃ in both cases. These reductions indicate that de novo-synthesis occurs at 320℃ when the ESP ash is added into the reaction system. The de novo-synthesis is more pronounced when the amount of ESP ash or the temperature of the reaction is increased, as this results in a reduction of the catalyst dioxin removal ability.

Meanwhile, the dioxin removal abilities of the PCDDs and PCDFs are also compared in Fig.2. This comparison shows that the difference in the dioxin removal ability between PCDDs and PCDFs became more pronounced as both the amount of ESP ash and the temperature of reaction were increased. The dioxin removal ability of PCDDs was better than that of PCDFs and this can be rationalized by the de novo-synthesis, which is more favorable to PCDFs formation. The degree of formation for PCDFs is about ten times that of PCDDs, which has been reported by Xhrouet et.al[2]. Thus, de novo-synthesis reduces the dioxin removal ability of PCDFs with ESP ash added substantially and it changes the profile of the dioxin-like congeners.

The effects of the ESP ash on the dioxin removal ability of the 17 different dioxin-like congeners are presented in Fig. 3(A) for PCDDs and in Fig. 3(B) for PCDFs, respectively. In Fig.3, it is shown that the sparsely chlorinated PCDD/Fs species had a better dioxin removal ability than that of the highly chlorinated PCDD/Fs species at 250℃, but that the difference in the dioxin removal ability between the sparsely and the highly chlorinated PCDD/Fs species became insignificant when the temperature was raised to 280~320℃. This can again be attributed to the de novo-synthesis, which is more favorable to the formation of sparsely chlorinated

PCDD/Fs species when the ESP ash is added in the reaction system at higher reaction temperatures. Due to the counter effect between the de novo-synthesis induced by the addition of ESP ash and the catalytic decomposition of dioxins by SCR catalyst, the difference in the removal ability between the sparsely and the highly chlorinated PCDD/Fs species is reduced significantly. The de novo-synthesis becomes more prominent when the ESP ash is increased to 0.2g. At 320℃, the dioxin removal ability of highly chlorinated PCDD/Fs species is expected to be higher than that of the sparsely chlorinated PCDD/Fs species. Thus, the de novo-synthesis, induced by the ESP ash and demonstrated in this study, will lower the ability of the SCR catalyst to remove dioxins.

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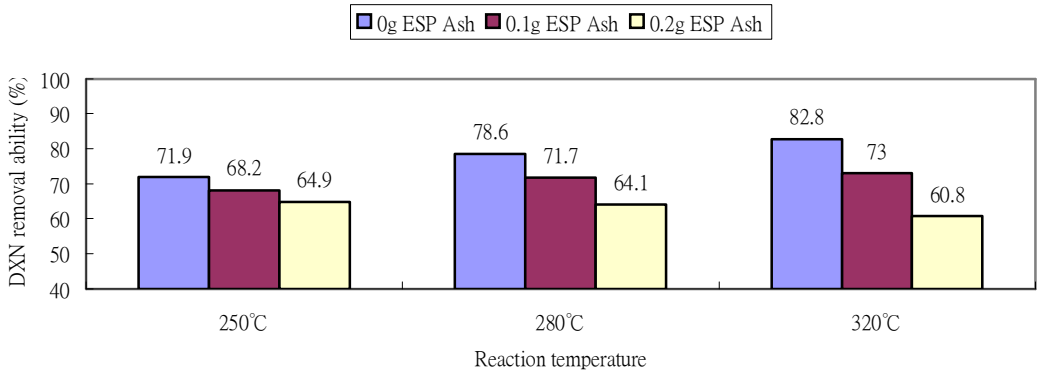

Fig.1.Dioxin removal ability as a function of ESP ash amount and operation temperature over the SCR catalyst

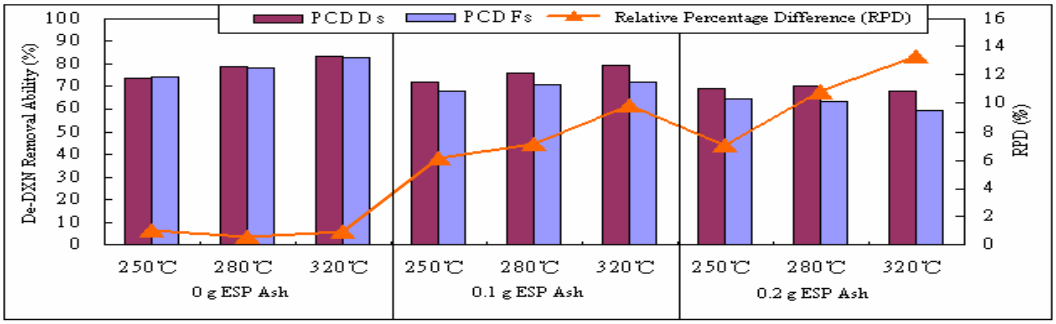

Fig.2. Effects of the ESP ash amount and the operation temperature on the dioxin removal ability of PCDDs and PCDFs congeners.

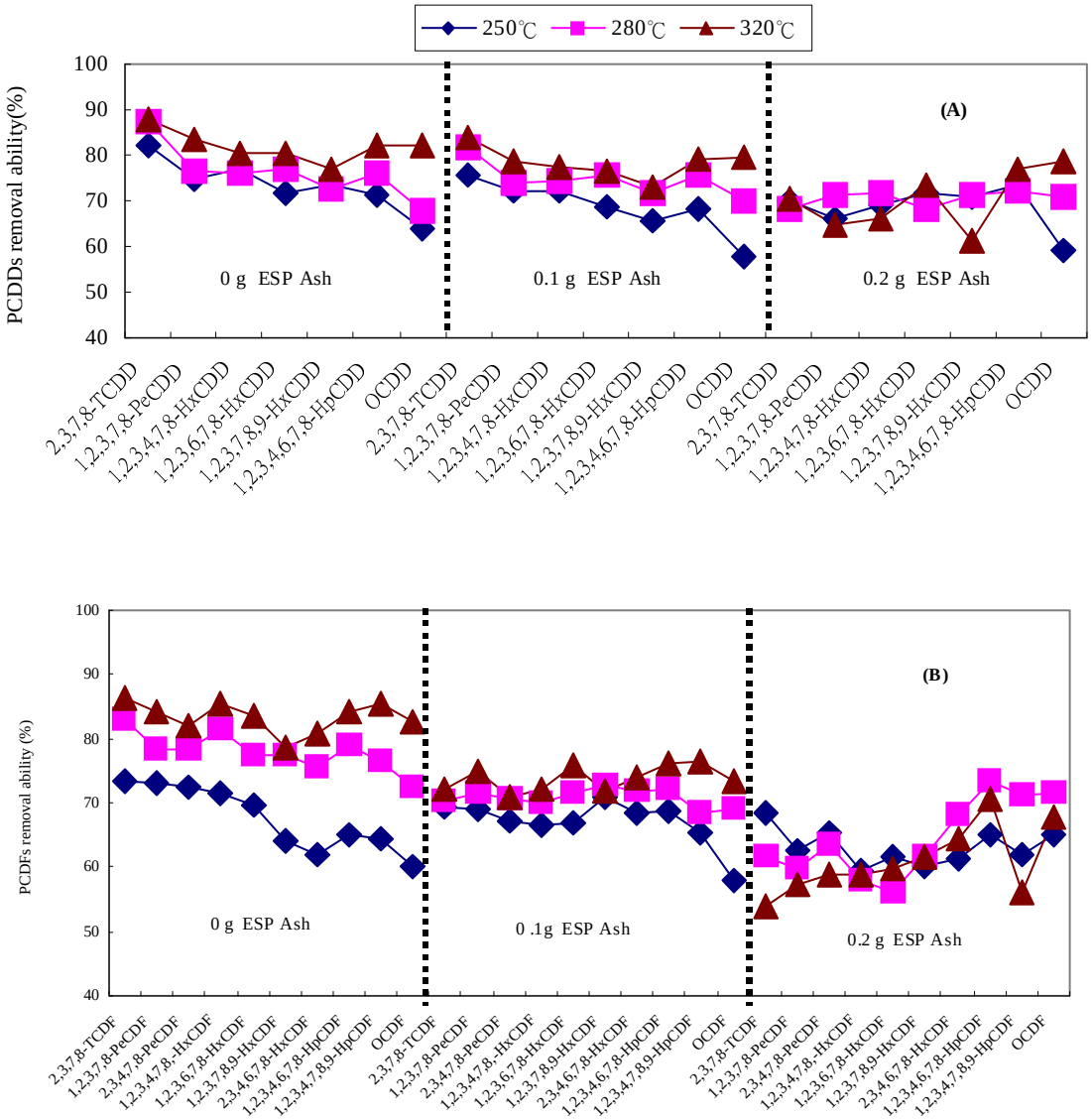

Fig.3. Effect of ESP ash on the dioxin removal ability of each species included in (A) PCDDs and (B) PCDFs congeners with respect to reaction temperature over the SCR catalyst.