Study on the formation of PCDD/Fs in PVC chemical looping combustion

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Abstract: CaSO₄ oxygen carriers with silica sol were prepared and their reaction performances with CH₄, CO and H₂ were experimentally investigated. The formation characteristics of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in PVC combustion by means of chemical looping combustion (CLC) based on CaSO₄ oxygen carrier and air were studied in a tube furnace system. The results show that CaSO₄ oxygen carriers with silica sol can be completely reduced by CH₄, CO and H₂. The reaction time of CH₄ and H₂ is much shorter than CO. The chemical looping combustion of PVC can effectively inhibit the formation of PCDD/Fs. The yield and International Toxicity Equivalent Quantity (I-TEQ) of PCDD/Fs produced in CLC are 2270.9 pg/g and 290.2 pg(I-TEQ)/g, much lower than those in air combustion which are 34172.5 pg/g and 732.8 pg(I-TEQ)/g. It is mainly because fuel doesn't directly contact with O₂ in CLC, the oxidative cleavage of large carbon molecule and the conversion from HCl to Cl₂ are significantly reduced which will inhibit the low temperature de novo synthesis and precursors reaction of PCDD/Fs.

Key Words: chemical looping combustion; PCDD/Fs; PVC; oxygen carrier; calcium sulfate

The disposal of combustible solid waste (CSW) is one of the severely environmental problems in the world^[1]. Composting, landfill and incineration are the common treatment methods of MSW. Incineration is the main developing direction in combustible solid waste management because of its small occupation area, stable and reliable operation and good reduction^[2]. But incineration of CSW is easy to produce PCDD/Fs and other toxic substances, which is harmful to human health. So its development is controversially^[3]. Hutzinger et al^[4] found that de novo synthesis and precursor reaction are the main generating ways of PCDD/Fs in CSW incineration. O₂ plays an important role in the two reactions^[5]. Therefore, avoiding the direct contact of O₂ and fuel is one of the feasible approaches to inhibit PCDD/Fs generation in combustion.

Chemical looping combustion (CLC) is a new combustion technology. The oxygen is transferred from air to fuel by means of the circulation of oxygen carriers between air reactor and fuel reactor, which realize the non-contact combustion of fuel and air^[6]. The formation of PCDD/Fs may be greatly inhibited by use of CLC to dispose CSW, because there is no direct contact between free oxygen and CSW.

Oxygen carriers are the key element in CLC. The metal oxides such as Ni, Cu, and Fe are mainly studied at present^[7]. However, metal oxides have strong catalysis on the formation of PCDD/Fs^[8], which may aggravate its generation. By contrast, CaSO₄ oxygen carrier is more suitable to dispose high chlorine CSW because of its high oxygen transport capacity, low cost, environmental friendliness and small catalysis on the formation of PCDD/Fs^[9].

Based on this, CaSO₄ oxygen carrier with silica sol is prepared and its reaction characteristics with different fuel gas were experimentally investigated. Finally, the influence of CLC and air combustion on the formation of PCDD/Fs is investigated by use of CaSO₄ oxygen carrier with silica sol and PVC.

1 Experimental

1.1 Materials and oxygen carrier preparation

Reagent: CaSO₄ (Sinopharm Chemical Reagent Co., Ltd.); silica sol (Qingdao Hengshengda Chemical Co., Ltd.); PVC (Sinopec Qilu Co., Ltd, Shandong, China).

Received: 15-Feb-2015; Revised: 06-May-2015.

Foundation item: Supported by the National Basic Research Program of China (973 program, 2011CB201502); China Postdoctoral Science Foundation Funded Project (2014M551978).

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Preparation method: CaSO_4 oxygen carrier was prepared by mechanical mixing method. First, silica sol and CaSO_4 were mixed together according to the same concentration. Then the mixture was dried at room temperature for 24 h and finally calcined at 900°C for 5 h. The content of CaSO_4 in the fresh oxygen carrier is 87%.

1.2 Characterization of oxygen carrier

Thermogravimetric analysis was carried out to study the reduction reactivity of oxygen carrier in a magnetic levitation thermogravimetric analyzer (RubothermDynerm-HP, Holland). First, 50 mg oxygen carrier was loaded in a crucible. Then the temperature was raised and maintained at 900°C in Ar atmosphere. Finally, 50 mL/min reducing gas (CH_4 , H_2 and CO , respectively) was introduced into the TGA to reduce the oxygen carrier.

The XRD analysis of oxygen carrier was carried out using Bruker D8 ADVANCE XRD system (Bruker) with $\text{Cu K}\alpha$ radiation (40 kV/40 mA). The scan range was from 5° to 75° with $2^\circ/\text{min}$ and the step stride is 0.02° .

1.3 Combustion and PCDD/Fs detection system

Both the combustion experiments of PVC and measurement of PCDD/Fs were carried out in the dioxin laboratory, Zhejiang University. Experiments were carried out in a tubular furnace (Figure 1) comprising three sections and featuring three independent heaters and temperature controllers (t_a , t_b , t_c). Quartz reaction tube consists of inner tube (i.d. = 20 mm, length = 400 mm) and outer tube (i.d. = 25 mm, length = 1000 mm). Two groups of experiments were conducted and repeated once. The experimental conditions are shown in Table 1. In the experiment, T_a and T_b were set at 900°C and T_c was room temperature. When the temperature reached set value, oxygen carrier was firstly loaded in the place 5 of inner tube and fixed by the quartz cotton. Then corresponding gas was introduced for 30 min to purge residual gas. Finally, the quartz boat with PVC was quickly pushed into place 3 of inner tube. The reaction time is 20 min.

The PCDD/Fs in exhaust gas was absorbed with XAD-2 resin and methylbenzene (ice-water bath) at the end of furnace. Then the exhaust gas was analyzed by Online Infrared Flue Gas Analyzer (FT-IR, Gas-met DX4000). The collected dioxins samples were sealed and analyzed by the dioxin laboratory, Zhejiang University.

The calculation formulas of relative generation of PCDD/Fs and I-TEQ are:

$$C_i = A_i / B \text{ (pg/g)} \quad (1)$$

$$Q_i = C_i \times F_i \text{ (pg(I-TEQ)/g)} \quad (2)$$

Where A_i , Q_i , C_i , F_i represent the detection quality, relative generation, I-TEQ and international toxicity equivalent factor

of i kind of PCDD/Fs respectively. B is the PVC quality of the corresponding experiment.

Fig.1 Diagram of PCDD/Fs experimental system

1: mass flow meter; 2: internal quartz tube; 3: quartz boat;
4: quartz cotton layers; 5: oxygen carrier; 6: long furnace;
7: external quartz tube; 8: XAD resin; 9: toluene; 10: ice bath

Table 1 Experimental conditions of dioxin

Experiment parameter	CLC	Air combustion
PVC m/g	1	1
CaSO_4 m/g	5	0
Atmosphere	N_2	Air
Gas flow rate $q/(\text{mL} \cdot \text{min}^{-1})$	200	200
Temperature $t/^\circ\text{C}$	900	900

2 Results and discussion

2.1 Reaction characteristics of oxygen carrier

Figure 2 shows the reduction reaction TGA curves of CaSO_4 oxygen carriers with silica sol in CH_4 , CO and H_2 atmosphere. Because the content of CaSO_4 in the fresh oxygen carrier is 87%, the actual oxygen transport capacity of the fresh oxygen carrier is 41%. As shown in Figure 2, all of the weight loss of CaSO_4 oxygen carriers with silica sol are 40% in three kinds of atmosphere which is very close to the theoretical value. This is because the oxygen carrier is almost completely reduced and CaSO_4 is converted into CaS . Few side reaction is occurred. The reaction is given by Eq. (3) – Eq. (5).

From Figure 2, it can be seen that the reaction time of CH_4 and H_2 is shorter, which are 15 and 20 min respectively. However, the reaction time of CO is more than 100 min. It is demonstrated that the reaction performance of oxygen carrier with CH_4 and H_2 is better than CO .

2.2 XRD characterization of oxygen carrier

Figure 3 shows the XRD analysis of oxygen carrier before and after reaction in three kinds of atmosphere. As shown in Figure 3(a), the main component of the fresh oxygen carrier is CaSO_4 . The inert component SiO_2 is amorphous. From Figure 3(b), the main components of reduced oxygen carrier are CaS and CaSiO_3 . According to the weight loss rate in section 2.1, CaS is in the majority and CaSiO_3 is formed by the co-product CaO and SiO_2 .

2.3 SEM characterization of oxygen carrier

Figure 4 shows the SEM analysis of oxygen carrier before and after reaction. As shown in Figure 4, the particle size of fresh CaSO_4 oxygen carrier is large and then decreases after reaction. The surfaces of oxygen carrier reduced by CH_4 and

H_2 are rough and porous. So the oxygen carrier can fully react with fuel gas which will reduce the reaction time. By contrast, the surface of oxygen carrier reduced by CO is smooth and has fewer pores. Thus, fuel gas is difficult to get inside of the oxygen carrier which increases the reaction time.

Fig.2 TGA curve of oxygen carrier under reductive atmosphere

Fig.3 XRD results of CaSO_4 oxygen carrier with Silica Sol

(a): fresh; (b): reduced

Fig.4 SEM images of CaSO_4 oxygen carrier with silica sol

(a): fresh; (b): reduced by CH_4 ; (c): reduced by CO ; (d): reduced by H_2

2.4 Formation characteristics of PCDD/Fs in PVC combustion

In order to study the completeness of PVC chemical looping combustion, the exhaust gas is firstly analyzed. Figure 5 shows the volume fraction profiles of exhaust gas in chemical looping combustion. As shown in Figure 5, the volume fraction of CO_2 increased gradually which means that Eq. (3) – Eq. (5) began to take place. The volume fraction of CO_2 reached the maximum of 8% at 14 min. Then it rapidly decreases and approached 0 at 17 min which means the end of reaction. During the whole reaction, the concentration of CO and CH_4 was less than 10^{-6} . It indicates that the chemical looping combustion of PVC is complete.

Fig.5 Exhaust gas volume fraction profiles in chemical looping combustion

Figure 6 and Figure 7 respectively show the generation and I-TEQ of toxic PCDD/Fs profiles in different PVC combustion methods. The data had taken the average of double repeated experimental results because the error is acceptable. As shown in Figure 6, in the air combustion of PVC, O8CDFs and H7CDFs were the major homologs of PCDD/Fs, and their proportion accounted for 86.2%. The total production of PCDFs was much higher than PCDDs and the ratio of PCDDs to PCDFs was 0.11. However, O8CDDs, H6CDFs and O8CDFs were the major homologs by use of CLC method and their proportion was 56.7%. The total production of PCDFs was close to PCDDs and the ratio of PCDDs to PCDFs was 0.83. From Figure 7, P5CDFs and

H6CDFs were the main source of I-TEQ in the air combustion, and their proportion was 73.9%. But in the CLC, P5CDDs was the biggest contributor to I-TEQ whose proportion accounted for 47.1%.

Table 2 shows the results of total PCDD/Fs and I-TEQ in different combustion methods. As shown in Table 2, the concentration of total PCDD/Fs and I-TEQ in chemical looping combustion were 2270.9 pg/g and 290.2 pg(I-TEQ)/g respectively, much lower than those in air combustion which were 34172.5 pg/g and 732.8 pg(I-TEQ)/g. It means the CLC method can effectively inhibit the formation of PCDD/Fs in PVC combustion.

Fig.6 Toxic PCDD/Fs homologue profiles for PVC combustion

Fig.7 I-TEQ of toxic PCDD/Fs homologue profiles for PVC combustion

Table 2 Results of PCDD/Fs and I-TEQ

Method	Content $w/(\text{pg} \cdot \text{g}^{-1})$			I-TED $w/(\text{pg(I-TEQ)} \cdot \text{g}^{-1})$
	PCDDs	PCDFs	PCDD /Fs	
CLC	1007.91	1263.022	2270.9	290.2
Air combustion	3570.886	30601.611	34172.5	732.8

2.5 Inhibition mechanism of PCDD/Fs in PVC chemical looping combustion

In waste incineration, PCDD/Fs generated by the mechanism of high-temperature pyrosynthesis is much less than that by low-temperature de novo synthesis and precursor synthesis, and can be ignored^[10]. According to the study of Buekens et al^[11] and Dickson et al^[12], most of the PCDDs are formed by precursor synthesis, and on the contrary PCDFs are mainly generated by de novo synthesis. Therefore, the dominant mechanism of PCDD/Fs formation could be determined by the ratio of PCDDs to PCDFs. When it is larger than 1, precursor synthesis is the predominant mechanism. And when it is smaller than 1, de novo synthesis is dominant. According to the analysis of section 2.4, both the ratios of PCDDs to PCDFs were smaller than 1 under two combustion methods. It means that PCDD/Fs were mainly generated by de novo synthesis in the experiment. The concentration of PCDFs was sharply decreased from 30601.611 pg/g (in air combustion) to 1263.022 pg/g (in CLC). And the total I-TEQ was also reduced from 67.1 pg(I-TEQ)/g (in air combustion) to 9.1 pg(I-TEQ)/g (in CLC). By contrast, the decrease of PCDDs in CLC was not obvious. It was about 1/3 of that in air combustion. And the I-TEQ of PCDDs formed in CLC was even higher than that in air combustion. Hence we infer that the chemical looping combustion method can effectively inhibit the de novo synthesis and it also has certain inhibitory effect on the precursor reaction. Thus the formation of PCDD/Fs could be significantly reduced in chemical looping combustion.

There are two possible reasons for above results. On one hand, the influence of O₂ on de novo synthesis is larger than precursor reaction. In the de novo synthesis, macromolecular carbon is cracked by the oxidation of O₂, and then the aromatic structure separates from macromolecular carbon and forms PCDD/Fs through condensation, cyclization and chlorination^[13]. But in CLC, fuel doesn't directly contact with O₂, so the large carbon molecule fracture is difficult to breakdown which will sharply reduce the PCDD/Fs formation by de novo synthesis.

On the other hand, chlorine source is necessary for both de novo synthesis and precursor reaction. Cl₂ is the most important chlorine source in the reaction^[14]. It mainly produced by HCl and O₂ via Deacon Reaction^[15]:

From Eq. (6), O₂ is the key of transformation from HCl to Cl₂. In the PVC chemical looping combustion, HCl produced from PVC can only contact with CaSO₄ instead of free O₂. Therefore, the production of Cl₂ is sharply reduced, so the chlorinated reaction is greatly weakened and the formation of PCDD/Fs is finally inhibited.

However, PCDD/Fs formation mechanism is much more complicated in actual combustion and the dominant reaction mechanism is still controversial. More experiments are needed to study the PCDD/Fs inhibition mechanism in chemical looping combustion.

3 Conclusions

CaSO₄ oxygen carriers with silica sol can be completely reduced by CH₄, CO and H₂, and the main product is CaS. Few side reactions are happened and CaSiO₃ is generated with SiO₂. The reaction time of CaSO₄ oxygen carriers with CH₄ and H₂ is shorter than that with CO.

The chemical looping combustion of PVC based on CaSO₄ oxygen carrier can effectively inhibit the formation of PCDD/Fs. The concentration of total PCDD/Fs and I-TEQ produced in CLC are 2270.9 pg/g and 290.2 pg(I-TEQ)/g respectively, much lower than those in air combustion which are 34172.5 pg/g and 732.8 pg(I-TEQ)/g. It is mainly because in CLC fuel doesn't directly contact with O₂, the oxidative cleavage of large carbon molecule and the conversion from HCl to Cl₂ are significantly reduced which will inhibit the low temperature de novo synthesis and precursors reaction of PCDD/Fs.

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