STUDY OF INHIBITION EFFECT ON DE NOVO SYNTHESIS OF PCDD/FS BY ONE N-P-CONTAINING COMPOUND VIA CARBON DECOMPOSITION AND KINETICS

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) are unintentional emissions during the incineration of municipal solid waste and other anthropic activities, and their emission is a severe issue for environmental safety and human health[1,2]. De novo synthesis was regarded as the most important pathway for the generation of PCDD/Fs in waste incinerators, which mainly happened at 300-400℃[3,4].

Previous studies showed that carbon decomposition derived from gasification/oxidation of carbon were related to the PCDD/Fs formation[5-7], and some scholars studied the kinetics of carbon decomposition/gasification associated with de novo synthesis[8-10]. Chemical inhibitors such as nitrogen-, sulfur-, phosphorus- as well as calcium-containing compounds have been applied to the suppression of PCDD/Fs, and proved capable of good inhibition effects[11-16]. However, research with respect to the relations between inhibition of PCDD/Fs and carbon gasification was limited. Many of the studies in PCDD/Fs inhibition concentrated on the inhibition effect and efficiency as yet, and some ever mentioned the inhibition mechanism of these inhibitors e.g. thiourea, urea[17,18]. Although it was reported that the effect of SO_2 on the oxidation of carbon related to de novo reaction[19], the corresponding relations of other inhibitors like N-, P- or Ca- containing compounds were unknown. Therefore, it is necessary to investigate the relations between the inhibitory reaction of de novo synthesis and carbon gasification/decomposition. The thermogravimetry (TG) was chosen to study the kinetics of carbon decomposition/gasification correlated to de novo synthesis in the present study, and the method was ever employed which seemed feasible[8]. However, the kinetics of carbon decomposition/gasification in previous studies was generally based on a first-order reaction, while the presence of $CuCl_2$ in fly ash might change the reaction model. Thus, Popescu and Friedman, KAS methods were employed to obtain a more appropriate and suitable reaction model[20,21].

The aim of this study was focused on the effect of inhibitors on the carbon gasification in de novo synthesis and the kinetic model by TG-FTIR. The temperature range in the present study was concentrated on 300-350℃, the main temperature window of de novo reaction. This study not only investigated the effect of Ammonium dihydrogen phosphate (ADP) on de novo synthesis, but also ADP was coupled with CaO to study the synergetic effect. The TG measurements carried out at several heating rates to determine the apparent activation energy and pre-exponential factor, as well as the most probable mechanism function.

2. Materials and method

2.1 Sample preparation

At the PCDD/Fs de novo synthesis experiments, the model fly ash (MFA-1), including 91.6% SiO_2, 3% activated carbon (AC), 5% NaCl and 0.4% $CuCl_2.2H_2O$, whose composition was similar to the actual waste incinerator fly ash. The model fly ash (MFA-2) used in TG-FTIR experiments was prepared by the mixture of 50% activated carbon (AC) and 50% $CuCl_2.2H_2O$. Ammonium dihydrogen phosphate (ADP) was chosen to be the inhibitor of PCDD/Fs de novo synthesis. The alkaline material CaO was also added into ADP (ADP+CaO) in a ratio 1:1 to investigate the synergetic inhibition effect. Besides, CaO alone was added to study the effect of CaO.

2.2 De novo synthesis of PCDD/Fs and the inhibition experiments

The experiments were conducted in a vertical tubular furnace previously described in detail by Lu et al[11]. At each test, 1g MFA-1 or 1g MFA-1+ 0.08g inhibitor was loaded in the quartz reactor, which was inserted in the furnace. Before the experiment, the furnace was heated up until the temperature stabilized at 350℃, and the quartz reactor loaded sample was placed inside to be heated for 60 minutes under the atmosphere of model flue gas (89 vol.% N_2+11 vol.%O_2) with the flow rate of 100 mL/min. The gaseous PCDD/Fs was absorbed by XAD-2 resin and toluene.

2.3 TG-FTIR experiments

The crucible contained about 20 mg of sample (90% MFA-2+10% inhibitor) was placed in a synchronous thermal analyzer (NETZSCH, Germany, STA449 F5), and introduced simulated flue gas (90% N_2+10% O_2). The crucible was heated from ambient temperature to 750 °C with heating rates of 10 K/min, 15 K/min and 20 K/min, and production gases were imported into a Fourier transform infrared spectrometer (VERTEX 70, Bruker, Germany) to analyze the decomposition products.

3. Results and discussion

3.1 Effect of inhibitors on PCDD/Fs formation and isomer distribution

Figure 1 showed that the inhibitors ADP, ADP+CaO and CaO had significant effects on PCDD/Fs formation. The inhibition efficiencies of ADP for total concentration and I-TEQ of PCDD/F were 98.45% and 96.55%, respectively. It was observed that the ratio of PCDF:PCDD was greater than 1, indicating the dominant reaction of de novo synthesis. In particular, ADP alone performed the best on toxic PCDF inhibition, whereas had a better inhibition effect on toxic PCDDs after coupling CaO (95.69%) than ADP (90.91%) or CaO (92.60%) alone. Figure 2 showed the isomer distribution of 17 toxic 2,3,7,8-substituted PCDD/Fs. CaO had a better inhibition effect on the formation of 2,3,7,8-TCDD (0.1139 ng/g) than ADP (0.2993 ng/g), while their cooperation acted the best (0.0938 ng/g) on the suppression of 2,3,7,8-TCDD (I-TEF=1) and PCDDs. Regarding PCDFs, the concentration of 2,3,4,7,8-PCDF (I-TEF=0.5) for the addition of ADP, ADP+CaO, CaO was 0.1036 ng/g, 1.0358 ng/g, 0.5383 ng/g, respectively. ADP alone performed the best for 2,3,4,7,8-PCDF inhibition, but the coupling of ADP and CaO acted the worst and promoted the total concentration of PCDFs. Thus, it could be concluded that ADP coupling CaO improved the inhibition efficiency on PCDDs formation but decreased that on PCDFs formation, thus the synergy of ADP and CaO might perform significantly on the reaction for the main production of PCDDs.

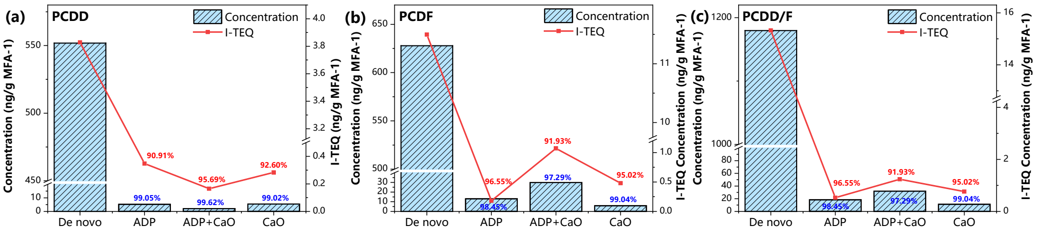

Figure 1. Influence of different inhibitors on the formation concentration and I-TEQ of 2,3,7,8-substituted PCDD/Fs

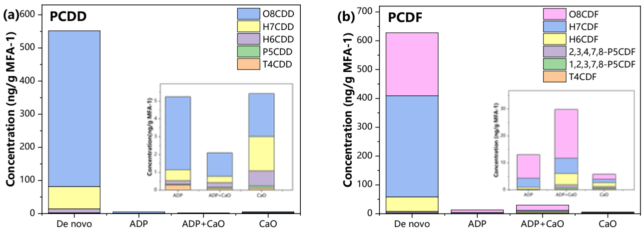

Figure 2. Influence of different inhibitors on isomer distribution of 2,3,7,8-substituted PCDD/Fs

3.2 Inhibition effect on carbon gasification

As was shown in figure 3(a, b), the temperature of maximum decomposition rate of model fly ash decreased a lot with the addition of $CuCl_2$ (from 650°C to 410°C), which illustrated the catalytic effect of $CuCl_2$ on carbon decomposition and gasification. The addition of ADP delayed the maximum decomposition of model fly ash (from 410°C to 495°C), and the synergy of ADP and CaO slightly reduced the temperature of maximum decomposition rate compared with ADP alone. It could be concluded that the presence of ADP indeed inhibited the decomposition of model fly ash. CaO promoted the decomposition of fly ash in the early stage (figure 3b), because CaO would absorb CO_2 to improve the carbon gasification. However, CaO inhibited the degradation of model fly ash during the late stage, most likely attributed to the absorption of HCl and Cl_2 by CaO[15,16].

The infrared absorbance intensity of CO_2 and CO reduced by 400%-500% with the addition of ADP at 300-350°C at 20K/min in figure 3 (c, d). It illustrated that ADP reduced carbon gasification rate of model fly ash in the temperature range of 300-350°C. However, the addition of CaO improved the production of CO_2 and CO compared to ADP. The infrared absorbance intensity of CO_2 and CO reduced by 400%-500% at 20K/min with the addition of ADP+CaO. CaO was well-known to be a kind of effective inhibitor of PCDD/Fs formation both in our experiment and others[15,16], thus we judged that the inhibition mechanism of de novo synthesis by CaO did not rely on the carbon gasification. Previous results suggested that P and N in ADP bound with Cu to deactivate the catalytic effect of $CuCl_2$. Results showed that $CuCl_2$ promoted the carbon gasification above, therefore we preliminarily judged that the passivation of Cu decreased the carbon gasification.

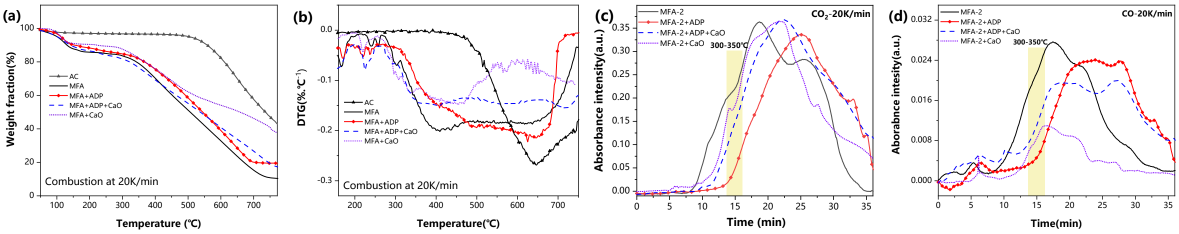

Figure 3. Influence of different inhibitors on TG, DTG and carbon gasification

(a) TG; (b) DTG; (c) Infrared intensity of CO_2 changing over time; (d) Infrared intensity of CO changing over time

3.3 Kinetic analysis

We obtained the most probable mechanism function by Popescu method, expressed as $f(\alpha)=2\alpha^{-1/2}/3$. It obeyed Mample power law, representing that this reaction was a phase boundary reaction consistent. De novo synthesis occurred on the surface of fly ash in the flue gas environment, which seemed consistent with the phase boundary reaction. The kinetic equation of the sample reaction could be expressed as $d\alpha/dt=A\exp(-Ea/RT)\cdot 2/3\alpha^{-1/2}$. As was shown in table 1, the apparent activation energy value increased with the addition of ADP and slightly decreased by the addition of CaO, corresponding to the performance of carbon gasification with the addition of inhibitors. It suggested that ADP inhibited the decomposition of model fly ash, mainly reflecting in the suppression of the carbon gasification, and CaO promoted the carbon gasification. *Ea* could be related to the energy of the bond formed. C-H bond was quite stronger than C-Cl[8], while the addition of ADP promoted the activation energy at 300-350°C, so it could be judged that ADP inhibited the formation of C-Cl and might more C-H remain stable. Table 2 provided a quantitative description of reaction rate by the kinetic equation above. The reaction rate decreased with the addition of ADP and increased with the addition of CaO, also illustrating that ADP suppressed carbon gasification and CaO promoted carbon gasification.

Table 1. Kinetic parameters by Popescu, Friedman and KAS methods at 300-350°C

Sample	**Popescu**			**Friedman**		**KAS**	
	***Ea*/(kJ.mol^{-1})**	***A*/s^{-1}**	***α***	***Ea*/(kJ.mol^{-1})**	***r***	***Ea*/ (kJ.mol^{-1})**	***r***
MFA-2	76.53	62107.54	0.07-0.11	71.05	0.994	78.50	0.969
MFA-2+ADP	95.15	680060.22	0.06-0.10	98.68	0.998	102.04	0.960
MFA-2+ADP+CaO	73.92	34550.53	0.08-0.12	67.80	0.981	70.60	0.994

Table 2. Calculation results of reaction rates by kinetic equation at 300-350°C

Sample	Reaction rate/(%.min^{-1})			Average value
	10K/min	15K/min	20K/min	
MFA-2	0.016659	0.019077	0.025552	0.0204293
MFA-2+ADP	0.013872	0.015387	0.016985	0.0154147
MFA-2+ADP+CaO	0.023523	0.019304	0.030241	0.024356

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