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Effects of SO_2 and SO_3 on the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans by de novo synthesis*

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Abstract: The effects of SO_2, SO_3 on de novo synthesis of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) were studied using model fly ashes incorporating copper oxide and activated carbon. It was found that the inhibitive effect of SO_2 on PCDD/Fs formation is similar to that of SO_3. To investigate the inhibition mechanism, $CuSO_4$ formations from both CuO and $CuCl_2$ were examined. The ability of SO_3 to convert $CuCl_2$ and CuO on a silica support into sulfate is much stronger than that of SO_2. However, replacing silica by activated carbon leads to a much high conversion of $CuCl_2$ to $CuSO_4$ in the presence of SO_2. The promotion by activated carbon is explained by the reduction of $CuCl_2$ to Cu_2Cl_2 and the eventual conversion of Cu_2Cl_2 into $CuSO_4$ is the main inhibition mechanism of SO_2 on de novo synthesis of PCDD/Fs.

Key words: Cuprous chloride, Model fly ash, Sulfation, Cupric chloride
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1 Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are unwanted by-products of combustion and many industrial processes (Ba *et al.*, 2009; Wang *et al.*, 2009). These compounds have been detected in the emissions of municipal waste incinerators (MWIs). Since they can be formed at lower temperature (250–400 °C) by de novo synthesis (Cunliffe and Williams, 2009), a feasible control method to reduce their emissions is to minimize their formation and remove PCDD/Fs formed.

Small amounts of PCDD/Fs were also detected in the emissions from coal fired combustors. Griffin (1986) proposed that the high sulfur content of coal was the cause of the low PCDD/F emissions from coal combustion. While the suppressant effect of high SO_2 concentrations on PCDD/F emissions is quite evident (Xu *et al.*, 2001), the inhibition mechanism of the SO_2 on PCDD/Fs formation by de novo synthesis remains elusive.

Considering that Cl_2 is potentially important in PCDD/Fs formation, Griffin (1986) proposed that the inhibiting effect of SO_2 is to deplete Cl_2 through the gas-phase reaction.

$$Cl_2+SO_2+H_2O\rightarrow 2HCl+SO_3. \qquad (1)$$

Raghunathan and Gullett (1996) also found about 30% conversion of Cl_2 to HCl at 400 °C in their experiment.

However, Gullett *et al*. (1992) proposed that SO_2 could deactivate the cupric oxide with a formation of cupric sulfate ($CuSO_4$).

$$CuO+SO_2+1/2O_2\rightarrow CuSO_4. \qquad (2)$$

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This conversion shifts the optimum temperatures for the Deacon reaction,

$$2HCl+1/2O_2 \rightarrow Cl_2+H_2O, \quad (3)$$

from ca. 390 °C to 500 °C. Addink and Altwicker (1998) found that copper in the form of $CuSO_4$ does not catalyse PCDD/Fs formation. Pekarek *et al*. (2007) found that reactions Eqs. (1)–(3) are thermodynamically possible at 300 °C according to their calculation. They also proposed that conversion of copper oxide/ chloride catalyst into the non-reactive sulfate was the main mechanism of SO_2 inhibition. According to their equilibrium calculation, they proposed that the formation of $CuSO_4$ is feasible by the following summary reaction:

$$SO_2+CuCl_2+H_2O+1/2O_2 \rightarrow CuSO_4+2HCl. \quad (4)$$

At 300 °C, Ryan *et al*. (2006) found that metal oxides (copper or iron) did not react with SO_2 to form metal sulfates under 10% O_2/8% H_2O/N_2. However, when 100×10^{-6} Cl_2 was added together with SO_2, significant amounts of metal sulfates were detected. They proposed that under oxidizing conditions metal sulfates were formed from metal chlorides and SO_2.

Lindbauer *et al*. (1994) investigated that the governing parameter is SO_3, not SO_2, and that PCDD/Fs formation is inhibited by masking the catalytic dust particle surface by sulphatization with SO_3. Pekarek *et al*. (2007) demonstrated that the inhibiting effect of sulfuric acid is more efficient than that of SO_2.

The objective of this study was to investigate the effects of SO_2 and SO_3 on de novo synthesis of PCDD/Fs using model ashes under controlled experimental conditions. The results show that both SO_2 and SO_3 have a strong inhibiting effect on PCDD/Fs formation. The nature of this effect is discussed. An inhibition mechanism is proposed according to the experimental results.

2 Experimental

2.1 Chemicals

Reagent-grade quartz powder (100–120 meshes) was first rinsed twice by distilled water, and then dried at 120 °C. It is called quartz sample [Q] in this study. Glass wool was cleaned by immersion in a diluted HNO_3 solution overnight, rinsed by distilled water, and then dried at 500 °C to remove organic compounds.

Reagent-grade V_2O_5, K_2SO_4, $CuCl_2\cdot2H_2O$, $Cu(NO_3)_2$ and activated carbon powder, pesticide-grade toluene, methanol, methylene chloride and acetone, high performance liquid chromatography (HPLC)-grade *n*-Hexane, diatomite were used. N_2 of 99.999%, O_2 of 99.995%, 950×10^{-6} SO_2 (the balance gas was N_2) and 900×10^{-6} Cl_2 (the balance gas was N_2) were supplied by the Jingong Gas Supplier, China.

2.2 SO_3 catalyst and sample preparation

SO_3 catalyst: an aqueous solution of K_2SO_4 and V_2O_5 was added to diatomite and exposed to an ultrasonic wave for 30 min (Tang *et al*., 1999). The impregnated diatomite thus obtained was then dried at 120 °C.

Model ash [$CuCl_2$]: an aqueous solution of $CuCl_2$ was added to [Q] and after impregnation the mixture was dried in a rotary evaporator and then dried at 120 °C. The Cu content in [$CuCl_2$] was 0.09% (w/w), the same order of magnitude as in MSWI fly ash.

Model ash [CuO]: an aqueous solution of $Cu(NO_3)_2$ was added to [Q] and after impregnation the mixture was dried in a rotary evaporator, then dried at 120 °C for 1 h and prepared by calcination at 480 °C for 16 h. The Cu content in [CuO] was 0.09%.

Model ash [AC]: 3 g activated carbon was added to 97 g [Q] and rotary mixed continuously for a week.

Model ash [$CuCl_2$+AC]: the water solution of $CuCl_2$ was added to activated carbon and after impregnation the mixture was dried in a rotary evaporator then dried at 120 °C. The Cu content in the mixture was 2.7%. 3 g mixture was added to 97 g [Q] and rotary mixed continuously for a week.

Model ash [CuO+AC]: 3 g activated carbon was added to 97 g [CuO] and rotary mixed continuously for a week.

2.3 Experimental procedure

Tests were run in a concentric tubular quartz reactor inserted into the horizontally mounted, 3-stage, electric furnace as shown in Fig. 1. The temperature of each stage was controlled by a single S type thermocouple. The first reactor stage was used for catalytically producing SO_3 and the temperature was set to 450 °C. The second stage was merely used as a mixing section and the temperature was set to 400 °C. The third stage was the reaction section proper.

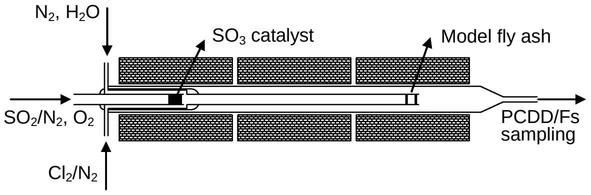

Fig. 1 Schematic of the reactor system

2.3.1 Effects of SO_2 and SO_3 on PCDD/Fs formation by de novo synthesis

The model ash [CuO+AC] was placed in the reaction section and was maintained by glass wool, and treated for 30 min at 350 °C in a flow containing either SO_2/Cl_2 or SO_3/Cl_2. A 400 ml/min flow of 300×10^{-6} $Cl_2/150\times10^{-6}$ SO_2/10% O_2/10% H_2O/N_2 was used for these experiments. When required, SO_3 was produced in situ by catalytic conversion of SO_2. The outlet gas from the reaction tube passed through an ice-cooled XAD-2 resinous column. The acetone, methylene chloride and toluene used for rinsing the inside of reactor, gas tubes and connecters were included in the PCDD/Fs analysis of the gas trap and residual ash. The EPA 1613 isotope dilution method was used for PCDD/Fs determination. Samples were analyzed by high-resolution gas chromatography/ high-resolution mass spectrometry (HRGC/HRMS) (JEOL JMS-800D) with a DB-5MS (60-m length, 0.25-mm inner diameter, 0.25-μm thickness film) column.

2.3.2 Investigation of $CuSO_4$ formation

The model ash was placed in the reaction section bounded by glass wool, and treated at 320 °C for 30 min in a flow containing SO_2 or SO_3. A 400 ml/min flow of 150×10^{-6} SO_2/10% O_2/10% H_2O/N_2 was used for these experiments. When required, SO_3 was produced from SO_2 by placing a 2 g SO_3 catalyst at the first stage. Before the experiments with SO_3, the SO_3 catalyst was thoroughly washed with the above gas for 12 h. The conversion into SO_3 was above 90% according to our measurement. After reaction, the model ashes were dissolved in diluted HNO_3 solution. Chlorine ion and sulfate ion contents in solution were analyzed by ion chromatography (Metrohm, 729 Basic IC).

3 Results and discussion

3.1 Effects of SO_2 on PCDD/Fs formation by de novo synthesis reactions

The effect of SO_2 on de novo synthesis is shown in Table 1. Figs. 2a and 2b illustrate the influences of SO_2 and SO_3 on PCDD/F homologue distribution. The results show the inhibitory effect of SO_2: in the presence of 300×10^{-6} Cl_2, the yield of PCDD/Fs is much higher when no SO_2 is added, but it decreases about 90.3% for an S/Cl ratio of 0.25 (mol/mol). However, homologue distribution and isomer profiles for each homologue (not shown) were less influenced by the SO_2 adding. These results imply that the addition of SO_2 affects the major formation pathway of the PCDD/Fs.

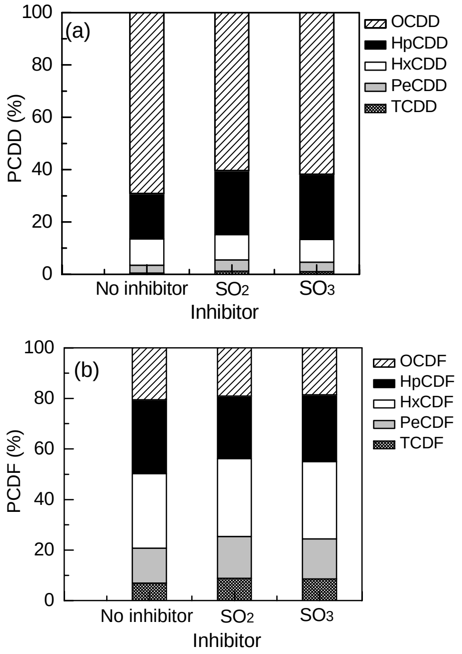

Fig. 2 Percentage of (a) PCDD and (b) PCDF homologue mass distributions of the samples with and without inhibitor during thermal treatment of model ash [CuO+AC] in laboratory scale experiments

The addition of SO_2 also shifts the PCDFs:PCDDs ratio from 1.94 to 3.2. In their model system, Pekarek *et al.* (2007) also reported a greater inhibiting effect of SO_2 on PCDD than on PCDF. It has been reported that several pathways exist in

Table 1 Effects of SO_2 and SO_3 on the formation of PCDD/Fs by de novo synthetic reactions (ng/g)

System	Test 1	Test 2[a]	Test 3	Test 4[b]	Test 5	Test 6[c]
	$CuO+Cl_2$	$CuO+Cl_2$	$CuO+Cl_2+SO_2$	$CuO+Cl_2+SO_2$	$CuO+Cl_2+SO_3$	$CuO+Cl_2+SO_3$
2378-TCDD	0.80	0.94	0.14	0.14	0.15	0.14
12378-PeCDD	3.8	3.9	0.64	0.71	0.61	0.57
123478-HxCDD	83	104	6.1	7.0	6.3	5.7
123678-HxCDD	80	85	3.5	4.1	4.0	3.4
123789-HxCDD	27	33	1.2	1.8	1.9	1.5
1234678-HpCDD	590	640	44	56	60	54
OCDD	4300	4700	230	310	330	300
TCDD	30	32	5.1	5.2	5.2	4.9
PeCDD	190	200	18	20	20	18
HxCDD	600	720	39	47	47	41
HpCDD	1100	1200	97	120	130	120
Sum of PCDDs	6200	6900	390	500	540	480
TEQ PCDDs	32	36	2.2	2.7	2.6	2.3
2378-TCDF	120	120	14	15	13	13
12378-PeCDF	73	75	6.9	7.2	6.0	6.0
23478-PeCDF	200	230	20	20	18	18
123478-HxCDF	460	480	36	37	34	32
123678-HxCDF	420	480	27	32	29	27
123789-HxCDF	370	430	31	34	32	29
234678-HxCDF	250	290	13	16	15	14
1234678-HpCDF	2800	3000	270	280	280	260
1234789-HpCDF	110	130	8.7	12	11	10
OCDF	2500	2700	260	280	250	240
TCDF	4300	4700	230	310	330	300
PeCDF	900	860	120	130	110	110
HxCDF	1700	1800	240	230	210	210
HpCDF	3500	3900	420	460	420	380
Sum of PCDFs	12000	13000	1400	1500	1400	1300
TEQ PCDFs	300	330	25	27	25	24
Sum of PCDD/Fs	18000	20000	1800	2000	1900	1800
Sum of TEQ PCDD/Fs	330	370	28	30	27	26
PCDFs/PCDDs	2.0	1.9	3.6	2.9	2.5	2.6

[a] repetition of Test 1; [b] repetition of Test 3; [c] repetition of Test 5

PCDD/Fs formation by de novo synthesis (Stieglitz *et al.*, 1997). The addition of SO_2 may reduce PCDD/F formation through one pathway more than via another pathway. This leads to the change of PCDFs:PCDDs ratio.

Ryan *et al.* (2006) found that the extent of Reaction Eq. (1) at 400 °C is too small to account for the extent of PCDD/F reduction. Gullett *et al.* (1992) and Telfer and Gullett (2002) also did not observe either homogeneous conversion of Cl_2 to HCl or depletion of SO_2 to form SO_3. Therefore, the conversion of copper catalyst into $CuSO_4$ in the model ash should be the main suppressant mechanism of SO_2 in these experiments.

3.2 Effects of SO_3 on PCDD/Fs formation by de novo synthesis reactions

The influence of SO_3 on de novo synthesis is illustrated in Table 1 and Figs. 2a and 2b. When both 150×10^{-6} SO_2 and SO_3 catalysts were added, a 90.5%

reduction in PCDD/Fs and a 92.4% reduction in PCDD/Fs TEQ emissions can be found from Table 1. These results are very close to those when only SO_2 was added. A minute effect on the homologue profile by SO_3 catalyst adding is also observed. The PCDFs:PCDDs ratio increases to 2.6.

It is proposed that the formation of $CuSO_4$ was also the inhibition mechanism of SO_3 on de novo synthesis of PCDD/Fs. The almost same inhibitive efficiencies and minor change of homologue profiles suggests that sulfation abilities of SO_2 and SO_3 on copper catalyst are close.

3.3 Investigation of $CuSO_4$ formation

To thoroughly understand the inhibition mechanisms of SO_2 and SO_3 on de novo synthesis, conversion of CuO and $CuCl_2$ to unreactive $CuSO_4$ is investigated. The results of $CuSO_4$ formation corresponding to the reactions of model ashes in the flow containing SO_2 or SO_3 are shown in Table 2, where the values are means of two experiments. After 30 min reaction in a flow of 10% O_2/10% H_2O/N_2, only 8% chlorine is left in the model ash [$CuCl_2$] (Test 1). The reason for chlorine decrease is the reaction of H_2O with $CuCl_2$.

$$CuCl_2+H_2O \rightarrow CuO+2HCl. \tag{5}$$

When 150×10^{-6} SO_2 was added, no $CuSO_4$ was formed in model ash [CuO] (Tests 5). This result suggests that the extent of the Reaction Eq. (2) is minor within the de novo temperature window, despite its thermodynamic feasibility. However, 5.5% copper in model ash [$CuCl_2$] is converted to $CuSO_4$ (Test 4). When the SO_2 concentration increased to 300×10^{-6}, the conversion to $CuSO_4$ also increased two times (Test 6). These results were in agreement with Ryan *et al*. (2006).

However, SO_3 can strongly sulphatize CuO and $CuCl_2$. When the SO_3 catalyst was added in the reactor, a significant amount of $CuSO_4$ was detected in [$CuCl_2$] (Test 8) and [CuO] (Test 9), the conversions were 51% and 31%, respectively. It was interesting that when SO_2 or SO_3 was added, the chlorine content in model ash [$CuCl_2$] was higher than the experiment without SO_2 or SO_3. This may explain why $CuCl_2$ was masked by $CuSO_4$ and inhibited to react with H_2O.

It seems that the large distance between the sulfation ability of SO_2 and of SO_3 on CuO and $CuCl_2$ cannot explain the entire observed almost similar inhibitive efficiencies of SO_2 and SO_3. There should be some other inhibition mechanisms for SO_2. However, it is noteworthy that copper catalyst only works when it makes contact with carbon. To understand the impact of carbon on $CuSO_4$ conversion, the

Table 2 Concentrations of chlorine and sulfate in residual ashes without inhibitor and with inhibitors at 320 °C (average value)

Test[a]	Model ash	Inhibitor	Chlorine concentration (mg/g)	Sulfate concentration (mg/g)[c]
0	[Q]	0	0.003	0.006±0.001
1	[$CuCl_2$][b]	0	0.082±0.003	0.004
2	[CuO]	0	0.000	0.003
3	[Q]	SO_2 (150×10^{-6})	0.003	0.005
4	[$CuCl_2$]	SO_2 (150×10^{-6})	0.142±0.008	0.074
5	[CuO]	SO_2 (150×10^{-6})	0.000	0.006
6	[$CuCl_2$]	SO_2 (300×10^{-6})	0.121±0.001	0.148±0.008
7	[Q]	SO_2 (150×10^{-6})+SO_3 catalyst	0.000	0.017±0.002
8	[$CuCl_2$]	SO_2 (150×10^{-6})+SO_3 catalyst	0.343±0.012	0.694±0.015
9	[CuO]	SO_2 (150×10^{-6})+SO_3 catalyst	0.000	0.413
10	[AC]	SO_2 (150×10^{-6})	0.023±0.001	0.062±0.006
11	[$CuCl_2$+AC]	0	0.269±0.006	0.048±0.007
12	[$CuCl_2$+AC]	SO_2 (150×10^{-6})	0.043±0.003	1.058±0.020

[a] All experiments: 30 min; 2.0 g model ash; all experiments are in duplicate, mean value±range is shown; no range for Cl^- or SO_4^{2-} is given if negligible (<0.001); [b] The chlorine concentration in model ash [$CuCl_2$] is 0.1%; [c] Sulfate concentration in model ash is 1.35 mg/g when conversion of $CuSO_4$ is 100%

support of $CuCl_2$ was replaced by activated carbon. 76% copper was converted to $CuSO_4$ in model ash [$CuCl_2$+AC] (Test 12). The chlorine content in residual ash was also reduced to a low level. This result clearly shows that activated carbon strongly affects the SO_2 sulfating the $CuCl_2$ and the inhibitive effect of SO_2 on de novo synthesis mainly takes place on the carbon.

The reason for the promotion of $CuSO_4$ formation from $CuCl_2$ by activated carbon was probably the reduction of $CuCl_2$ by activated carbon. Takaoka *et al.* (2005) demonstrated that copper compound with a low valence was observed in real fly ash and model ash containing activated carbon at 300 °C under 10% O_2/90% N_2. However, no low-valence copper compounds were observed when the carbon in fly ash was removed. Therefore, we assumed that the reduction of $CuCl_2$ to Cu_2Cl_2 by carbon and then reacting with SO_2 and O_2 to form $CuSO_4$ were concluded to be the main $CuSO_4$ formation mechanism (Stieglitz *et al.*, 1989; Weber *et al.*, 2001).

$$2CuCl_2+ArH\rightarrow Cu_2Cl_2+ArCl+HCl, \tag{6}$$

$$Cu_2Cl_2+SO_2+O_2\rightarrow CuCl_2+CuSO_4. \tag{7}$$

The mechanistic steps taking place during de novo formation were proposed by Stieglitz *et al.* (1989; 1991): (1) the transfer of chloride to carbonaceous particulate material with formation of C-Cl bonds, and (2) the oxidation of the macromolecular structure carbon to carbon dioxide with releasing the PCDD/Fs, polychlorinated biphenyls (PCBs) as side products. The mechanism of the first step was proposed and demonstrated (Stieglitz *et al.*, 1989; Weber *et al.*, 2001). However, the mechanism of the second step remains unclear. Addink and Altwicker (1998) found that no PCDD/Fs were formed in a mixture of *o*-dichlorobenzene soot and CuO at 350 °C under air despite the presence of C-Cl bonds. It suggested the importance of copper chloride in the second step of de novo synthesis. Takaoka *et al.* (2005) reported that only low-valence copper compounds were observed in model fly ash containing activated carbon at 300 °C under 10% O_2/90% N_2. It is concluded that the catalyst of the second step is Cu_2Cl_2 but not $CuCl_2$. According to these results, we can conclude that the conversion of Cu_2Cl_2 to $CuSO_4$ (Reaction Eq. (7)), thus reducing the sites responsible for oxidation reactions is found to be the main inhibition mechanism of SO_2.

4 Conclusion

The inhibitive effects of SO_2 and SO_3 on de novo synthesis are almost the same as in our laboratory model system. While SO_2 has little apparent effect upon the conversions of $CuCl_2$ which are both on the silica to $CuSO_4$, the presence of SO_2 with SO_3 catalyst results in much higher conversions of $CuCl_2$ even of CuO to $CuSO_4$. Obviously, the conversion of $CuCl_2$ to $CuSO_4$ does not contribute to the reduced PCDD/Fs emissions. The greater conversion of $CuCl_2$ to $CuSO_4$ by activated carbon suggests that the inhibitive effect of SO_2 on de novo synthesis mainly takes place on the carbon. The reduction of $CuCl_2$ to Cu_2Cl_2 is ascribed to the effect of activated carbon on conversion. And $CuSO_4$ is formed from Cu_2Cl_2 and SO_2 with O_2. The conversion of Cu_2Cl_2 into $CuSO_4$ was concluded to be the main inhibition mechanism of SO_2.

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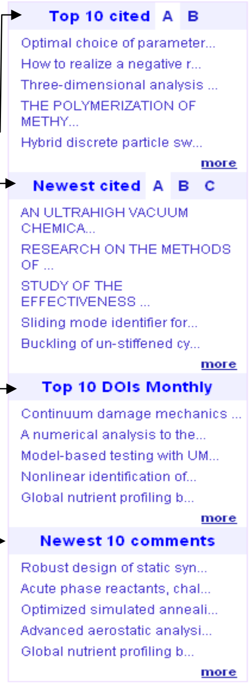
We also list the International Reviewers to express our deep appreciation and Crosscheck information etc.

If you would like to allot a little time to open http://www.zju.edu.cn/jzus, you will find more interesting information. Many thanks for your interest in our journals' publishing change and development in the past, present and future!

Welcome to comment on what you would like to discuss. And also welcome your interesting/high-quality paper to *JZUS(A/B/C)* soon.



Top 10 cited A B

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Top 10 DOIs Monthly

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A numerical analysis to the...
Model-based testing with UM...
Nonlinear identification of...
Global nutrient profiling b...
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Newest 10 comments

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