Synergetic inhibition of thermochemical formation of chlorinated aromatics by sulfur and nitrogen derived from thiourea: Multielement characterizations

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**HIGHLIGHTS**

- Inhibition effects and mechanisms of chlorinated aromatics formation by thiourea ([NH\textsubscript{2}]\textsubscript{2}CS) was investigated.
- PCDD/Fs, PCBs, and chlorobenzenes were inhibited effectively in the model/real fly ashes in the presence of thiourea after heating at 300°C.
- Multielement characterization using X-ray absorption spectroscopies of copper, chlorine, sulfur, nitrogen, and carbon revealed possible inhibition paths.
- Thiourea possibly influenced to sulfidization of the copper catalyst, blocking the chlorination of carbon, and changing the carbon frame.
- Thiourea plays a role as a sulfur and nitrogen donor to achieve multiple and synergistic inhibition of chlorinated aromatics.

**ABSTRACT**

Nitrogen and sulfur (N/S)-containing compounds inhibit the formation of polychlorinated dibenzo-p-dioxins (PCDDs) and furans (PCDFs) in thermal processes. However, few studies have examined the inhibition mechanisms of N/S-containing compounds. In the present study, we focused on thiourea ([NH\textsubscript{2}]\textsubscript{2}CS) as such a compound and investigated its inhibition effects and mechanisms. The production of PCDD/Fs, polychlorinated biphenyls (PCBs), and chlorobenzenes (CBzs) were inhibited by >99% in the model fly ash in the presence of 1.0% thiourea after heating at 300°C. Experimental results using real fly ash series were indicative of the thermal destruction of these chlorinated aromatics by thiourea. Multielement characterization using K-edge X-ray absorption fine structures of copper, chlorine, sulfur, nitrogen, and carbon revealed three possible inhibition paths, namely, (a) sulfidization of the copper catalyst to CuS, Cu\textsubscript{2}S, and CuSO\textsubscript{4}; (b) blocking the chlorination of carbon via the reaction of chlorine...
with N-containing compounds to generate ammonium chloride and other minor compounds; and (c) changing the carbon frame involved in attacking the carbon matrix by sulfur and nitrogen. Thus, thiourea plays a role as a sulfur and nitrogen donor to achieve multiple and synergistic inhibition of chlorinated aromatics. Our results suggest that other N/S-containing inhibitors function based on similar mechanisms.

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1. Introduction

Toxic chlorinated aromatic compounds (aromatic-Cls) such as polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs), biphenyls (PCBs), and benzenes (CBzs) are concentrated in fly ash during various anthropogenic thermal processes. Municipal solid waste incineration (MSWI) is a well-known source of aromatic-Cls, and unburned carbon, chlorine, oxygen gas, and trace metal compounds are key elements in generating aromatic-Cls [1–5]. Thus, technologies that inhibit their formation are required at thermal facilities to reduce the exhaust of aromatic-Cls, and using these technologies, we can prevent their toxic and detrimental environmental effects.

Among various chemical inhibitors, some nitrogen (N)- and sulfur (S)-containing compounds (hereafter, N/S-containing compounds) are known to inhibit aromatic-Cls formation during MSWI. Samaras et al. reported that N/S-containing compounds such as amidosulfonic acid (H2NSO2H), sulfamide (H2NSO2NH2), and hydroxylamine-O-sulfonic acid (H2NOSO2OH) have stronger inhibition effects on the formation of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) than urea, elemental sulfur, and mixtures of urea and elemental sulfur based on heating experiments of refuse-derived fuel (RDF) mixed with the inhibitors [6]. Pandelova et al. tested 20 different chemical inhibitors of aromatic-Cls in a laboratory-scale MSWI and found that ammonium sulfate [(NH4)2SO4] and ammonium thiosulfate [(NH4)2S2O3] were the most effective at preventing the formation of PCDD/Fs in fly gas [7]. These previous studies imply that N and S contained in “one” chemical structure may be an important factor to inhibit aromatic-Cl formation compared with N and S admixed separately. If we understand the inhibition mechanisms by N/S-containing compounds, effective inhibition techniques can be developed. However, no studies have examined the mechanisms by which N/S-containing compounds inhibit the formation of aromatic-Cls.

Urea [(NH2)2CO] contains nitrogen in its structure and is a known inhibitor of PCDD/Fs. Previous reports applying urea for various thermal processes showed that the inhibition effects of PCDD/Fs by urea ranged from 11 to 94% [6.8–14]. Additive percentages of urea (0.05–10%) increased the inhibition effects. Ruokojärvi et al. reported no inhibition effect by urea after a short combustion for 4 s of RDF in the presence of urea solution [15]. The inhibition effect by urea was lower than that by the N/S-containing compounds described above [6]. Two major urea inhibition mechanisms were proposed: (i) Direct interaction between copper catalyst and urea or its pyrolysis products [ammonia (NH3), HNCO] to inhibit PCDD/Fs formation [10,12] and (ii) hydrogen and/or chlorine combined with PCDD/Fs were substituted by nitrogen-containing groups derived from urea, which inhibit PCDD/F formation [13,14]. Based on these previous reports, thiourea [(NH2)2CS] (in which the oxygen in urea is displaced by sulfur, and nitrogen and sulfur are present in the structure) may have strong inhibition effects, similar to other N/S-containing compounds. In addition, the inhibition mechanisms of urea are suggestive of similar inhibition paths by thiourea.

Thermal decomposition of thiourea was well studied by Wang et al. [16] Isomeric reactions are thought to take place at 171.2–187.5 °C:

\[
SC(NH2)2(s) + \text{Heat} = NH4SCN(s) \quad \text{(R1)}
\]

According to the online Fourier transform infrared (FT-IR) spectra, carbon disulfide (CS2), isothiocyanic acid (HNCs), and NH3 were thermally decomposed from thiourea at 187.5–246.2 °C via the following two steps [16]:

\[
2SC(NH2)2(s) \rightarrow CS2(g) + H2NCN(g) + 2NH3(g) \quad \text{(R2)}
\]

\[
NH4SCN(s) \rightarrow NH3(g) + HNCs(g) \quad \text{(R3)}
\]

These thermal decomposition products from thiourea have potential to inhibit aromatic-Cls formation.

Based on previous reports, we hypothesized that thiourea may be an effective inhibitor. In the present study, we investigated the inhibition effects and mechanisms of thiourea during the thermochemical formation of aromatic-Cls in MSWI fly ash. PCDD/Fs, PCBs, and CBzs in model and real fly ashes (MFA and RFAs, respectively) were quantified using gas chromatography–mass spectrometry (GC–MS). To explore the inhibition mechanism by thiourea, we characterized various elements (Cu, Cl, S, N, and C) and copper catalysts using synchrotron-based X-ray absorption spectroscopy.

2. Materials and method

2.1. Sample preparation

We collected RFA as “raw” fly ash from an electrostatic precipitator at an MSW incinerator in Japan; the fly ash had not been sprayed with activated carbon (AC) or hydrated lime. The approximate contents of the study-related main elements in the RFA, as determined in our previous report, were (%): C: 8.3; Cl: 13; O: 28; Ca: 21; Na: 5.2; K: 5.2; Cu: 0.2; Fe: 1.7; Pb: 1.0; Zn: 4.2; and total organic carbon (TOC): 3.2 [17]. According to composition of the RFA, we also prepared an MFA that was a mixture of cupric chloride dehydrate (CuCl2·2H2O) or cupric chloride (CuCl2) as a representative metal catalyst, NaCl as a Cl source, AC, and a base material such as silicon dioxide (SiO2). Before performing the experiments, any organic compounds in the AC were removed by heating at 500 °C for 60 min under a stream of 100% nitrogen gas (100 ml/min) [18]. Then thiourea was added in the RFA and MFA by mixing in a mortar to characterize the inhibition effect. Additive ratio of thiourea was shown in Table S1. According to previous studies [19,20], we selected SiO2 as a representative base material to prepare the MFA. We purchased SiO2 (special grade), CuCl2 (98%, special grade), CuCl2·2H2O (99%, special grade), and NaCl (99.5%, special grade) from Nacalai Tesque (Kyoto, Japan), thiourea [(NH2)2CS, 99%, special grade] from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and AC [Shirasagi palm shell, 20–48 mesh (number of holes/inch)] from Takeda Pharmaceutical Co., Ltd. (Osaka, Japan). Detailed data on the samples are described in Table S1.

2.2. Measurement of chlorinated aromatic compounds

We placed 5 g of sample (RFA or MFA) into a quartz boat contained within a quartz tube (120 cm × 4 cm internal diame-
ter), which was then placed in a preheated electronic furnace at 300 °C for 30 min under a flow of 10% oxygen/90% nitrogen (O₂/N₂) delivered at 50 ml/min to simulate the post-combustion zone of an MSW. After heating, the concentrations of aromatic-ClS in the sample residue and in the gas phase collected in an impinger containing 100 ml of toluene were analyzed separately. The concentrations of PCDDs and PCDFs were assessed using high-resolution GC–high-resolution MS (HRGC–HRMS) [21]. In this study, PCBs and CBzs were analyzed using HRGC–low-resolution MS (GC-2010/GCMS-QP2010). Sample pretreatment for the determination of aromatic-ClS was performed according to Japanese Industrial Standards (JIS) K 0311 and 0312. For each heating experiment, analyses of the PCBs and CBzs were duplicated (n = 2). Recovery ratios of this methodology ranged 80–110%. Duplicated results showed good reproducibility of congener profile. Median variabilities of PCBs and CBzs among all congeners were under 20%, respectively. So, this methodology ensured reproducibility and relative small variability. Previously, the concentrations of PCDDs and PCDFs such as seventeen 2,3,7,8-substituted isomers in an MFA containing CuCl₂-2H₂O (MFA-Cu) were measured three times (n = 3) to confirm reproducibility [19]. The concentrations of aromatic-ClS from the MFA-Cu showed small deviations of the same order as those from an MFA of a similar composition reported by Stiegitz et al. [22]. In addition, coefficients of variance of aromatic-ClS isomer concentrations were also small [19]. It confirmed that our analytical procedures were reliable. Subsequently, concentrations of PCDDs and PCDFs in samples were measured once (n = 1). Total concentrations (sum of residue and gas phases) of PCDDs/Fs, PCBs, and CBzs from MFAs and RFAs are shown in Table S2.

2.3. X-ray absorption spectroscopy (Cu, Cl, S, N, and C)

X-ray absorption fine structures of Cu, Cl, S, N, and C K-edge were measured using an MFA containing AC (50%) and CuCl₂ (50%) with 100% thiourea [i.e., AC:CuCl₂:thiourea = 1:1:2, named MFA-T(X)], as shown in Table S1. Molar ratios of MFA-T(X) were 35% C, 33% H, 17% N, 8% S, 5% Cl, and 0.37% Cu. Weight ratios of MFA-T(X) were 33% C, 27% H, 18% N, 21% S, 13% Cl, and 12% Cu, which were then used to detect the analyzable spectrum of each element. Based on previous studies, MFA-T(X) did not include a Cl source (NaCl) or base material (SiO₂) to examine the behavior between the inhibitor and copper and to avoid the influence of the Si K-edge on the baseline of the Cl and S K-edge, respectively [23]. To avoid oxidation, MFA-T(X) was heated at 200, 300, or 400 °C for 30 min, and then immediately sealed for measurement of X-ray absorption spectroscopy. Detailed methods of X-ray absorption fine structures were described in Supplemental material.

Cu K-edge X-ray absorption near-edge structure (XANES) was performed using beamline BL01B1 at SPring-8 (Hyogo, Japan). The energies were first adjusted using the reference copper foil. The spectra of reference Cu compounds were measured to compare their spectral shapes and to identify major species. Species can be distinguished using the linear combination fit (LCF) technique. We conducted the LCF of the XANES spectrum to identify the major species using REX 2000 ver. 2.5.5 software (Rigaku, Tokyo, Japan). The residual value, R = Σ|XANES(meas) − XANES(cald)|^2/Σ|XANES(meas)|^2, was used to evaluate the LCF for the experimental spectra [24]. Cl and S K-edge near-edge X-ray absorption fine structure (NEXAFS) were performed using beamline BL-11B and BL-9A at the Photon Factory (Tsukuba, Japan). We corrected the energy position of the Cl K-edge using the absorption edge of KCl at 2822.8 eV [25]. The spectra of reference Cl materials were measured to perform the LCF analysis. S K-edge NEXAFS spectra were calibrated against the intense absorption feature of K₂SO₄ at 2480 eV [26,27]. The reference S compounds were measured. Various S K-edge NEXAFS spectra were based on previous reports [28]. We used peak positions derived from S-bonding structures based on these previous reports [29,30]. Energy areas containing these peak positions from 2469 to 2474 eV could be used as a fingerprint of the sulfur state bonding with the carbon matrix. N and C K-edge NEXAFS were performed using beamline BL-11A at the Photon Factory. The 0.5-mm-thick indium plate (99.995% purity: Nilaco Corp, Tokyo, Japan) was cut to an appropriate size and powder samples were mounted on the indium plate. NEXAFS spectra were collected by total electron yield (TEY) under high vacuum (10⁻⁶ Torr). We measured the N K-edge using an 800-l/mm holographic grating [31], Boron nitride (BN) at 408.1 eV (σ* transition) was used for energy calibration of N K-edge NEXAFS [32]. Reference N compounds were measured, as well as contaminated nitrogen in the AC. 400–401 eV and 407–411 eV of the N K-edge were indicative of the 1s → σ* transition and 1s → σ* C−N state transition, respectively [33,34]. In addition, Amano et al. showed the energy region at 397–401 eV as a representative fingerprint [35]. A holographic grating (300 l/mm) used for C K-edge measurement decreased the photocurrent intensity in the energy region of the C K-edge [31]. We addressed this problem by measuring the C K-edge region of a pure silicon wafer without carbon contamination and by correcting for inlet intensity (I₀). Thiourea and AC were selected as reference C compounds. Previous studies reported the 1s → σ* C=C transition at 284–287 eV and 1s → σ* C=C transition at 292–295 eV [36,37]. In addition, specific energy regions at 287–288 eV of the C K-edge are known to indicate 1s → σ* C=S, C=N, and C=O resonances [34,36–39]. We also analyzed functional groups by FT-IR based on our previous method [40] (see Supplementary material).

3. Results and discussion

3.1. Inhibition effect of thiourea on aromatic-ClS formation

We confirmed the inhibition effects of thiourea. The addition of 1.0% thiourea to MFA (MFA-T) resulted in an increased inhibition of aromatic-Cl formation compared to the no inhibition model (MFA-Cu), with a reduction in PCDDs, PCDFs, PCBs, and CBzs postheating by 99.98%, 99.97%, 99.7%, and 99.4%, respectively [Fig. 1A]. WHO-TEQ concentrations of PCDDs, PCDFs, and Co-PCBs in MFA-T were reduced by 99.79%, 99.98%, and 98%, respectively, compared to that by MFA-Cu. The inhibition effect to MFA system by thiourea showed higher than that by sulfur dioxide gas in our previous study [41]. Thus, thiourea effectively inhibited toxic congener formation from aromatic-ClS. MFA-T showed the same concentrations of PCDD/Fs, PCBs, and CBzs as the model containing no copper catalysts and no thiourea (MFA-B), which indicated deactivation of the copper catalyst by thiourea. Normalized distribution patterns of MFA series indicated that thiourea changed to lower congener profiles of aromatic-Cl compared to the Cu catalyst model (Fig. 2A). Distributions of PCDDs and PCDFs in MFA-T had lower patterns than that in MFA-Cu. In particular, PCB and CBz patterns in MFA-T differed from that in MFA-Cu, but were quite similar to that in MFA-B. Highly chlorinated patterns of aromatic-ClS were characteristic of the influence of the copper catalyst [19,20]. The influence of thiourea on the catalytic behavior of copper was supported by the lower tendency of congener distribution patterns of aromatic-ClS compared with MFA-Cu.

Aromatic-ClS in RFA were also inhibited by thiourea. Fig. 1B shows that the addition of 1.0% thiourea to RFA (RFA-T) decreased the concentration of PCDDs, PCDFs, PCBs, and CBzs by 61%, 83%, 29%, and 74%, respectively, compared with a system lacking thiourea (RFA-H). WHO-TEQ concentrations of PCDDs, PCDFs, and Co-PCBs in RFA-T decreased by 70%, 84%, and 72%, respectively, from that in RFA-H. Toxic congeners of PCDD/Fs showed a similar reduction.
3.2. Thermochemical behaviors of Cu, Cl, S, N, and C

The Cu K-edge XANES spectrum changed at each temperature, as shown in Fig. 3A. Spectral shapes at room temperature (rt) were relatively similar to CuCl. The LCF result indicated CuCl₂ as the major copper form (60%) and CuCl as the minor form (40%), as shown in Fig. 3B. Thus, copper maintained its chloride form via mixing of AC and CuCl₂, but was partly reduced from CuCl₂ to CuCl. The spectrum of the Cu K-edge changed dynamically at 200 °C and the absorption edge moved to a lower energy.

The spectral shape was similar to CuS. Ratios of chemical forms were 65% CuS and 35% Cu₂S. The majority of copper was sulfurated thermally as temperatures increased from rt to 200 °C in the presence of thiourea, after which chloride bonding with copper was released. According to reactions R2 and R3, decomposing

Note that toxic concentrations of Co-PCBs showed a more effective inhibition than the total amount of PCBs. Moreover, the concentrations of aromatic-Cls in RFA-T were lower than the concentrations of aromatic-Cls in the original raw RFA (Fig. 1B). Normalized distribution patterns of PCDD/Fs, PCBs, and CBzs in RFA-T showed the lowest chlorination patterns among the three RFAs (Fig. 2B). The RFA showed representative distribution patterns of these aromatic-Cls in MSWI fly ash [19]. RFA-T showed larger D2 biphenyls and D2 benzene in the distribution patterns than the RFA-H. Therefore, thermal dechlorination may occur in the presence of thiourea in case of PCBs and CBzs.

We measured amount of aromatic-Cls in gas phase by using toluene trap (Table S3). Inhibition effect by thiourea was found both in model and real fly ashes. So, homogeneous formation of aromatic-Cls was also inhibited by addition of thiourea. Although it is difficult to identify the formation paths (de novo or precursor), the PCDD/PCDF ratio (0.57–1.1) implied that de novo formation occurred mainly in gas phase [42].
S-containing products such as CS₂(g) and HNCS(g) were generated from thiourea at ~200 °C [16]. Thus, these compounds may react thermally with copper chlorides. Thermodynamic calculations using FactSage software revealed that hydrochloride (HCl) and chlorine (Cl₂) gases were produced through such reactions under the presence of oxygen or water vapor. Fig. S1 and S2 show the temperature dependence of change in Gibb's free energy (ΔG). Detailed results of thermodynamic calculations are described in Supplementary material. The spectral shape grew its broad peak at 300 °C (Fig. 3A). According to the LCF, the majority of the chemical form was Cu₃S (40%) and a minor part was oxidized CuO (23%), as shown in Fig. 3B. Some copper chlorides (17% CuCl₂ and 21% CuCl) were present at 300 °C. The re-chlorination of copper may be derived from thermal decomposition, such as NH₄Cl described below (ref. Fig. 4). At 400 °C, the spectral shape of the Cu K-edge showed a clear peak at 8995 eV. Chemical forms were mainly Cu₃S (51%), CuSO₄ (29%) and CuO (20%) were also identified by the LCF analysis. These results were suggestive of oxidation and sulfidization of copper as the temperature increased from 200 to 400 °C.

The thermochemical behavior of Cl was identified based on measurement and analysis of the Cl K-edge NEXAFS. The spectrum at rt showed characteristic pre-edge and white lines, which appeared in the CuCl₂ spectrum (Fig. 4A). A total of 73% and 27% of chlorine were identified as CuCl₂ and CuCl according to the LCF analysis (Fig. 4B). The pre-edge vanished and the peak shape was similar to NH₄Cl at 200 °C. The LCF result showed that the majority of chlorine was contained in NH₄Cl (71%), and 29% of the chlorine was identified as hydroxyamine hydrochloride (NH₄OH·HCl). NH₃ gas was thermally decomposed from thiourea at 188–246 °C via reactions (R2) and (R3) [16]. In addition, Cl-containing gases, HCl(g) and Cl₂(g), were released from copper as temperatures increased from rt to 200 °C based on Cu K-edge XANES (ref. Fig. 3). Therefore, NH₄Cl was generated thermally in the solid phase through the following reactions:

\[
\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl(s)} \text{at} 0\text{–}330 \degree \text{C} \quad \text{(R4)}
\]

\[
4\text{NH}_3(g) + 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g) \rightarrow 4\text{NH}_4\text{Cl(s)} + \text{O}_2(g) \text{at} 100\text{–}330 \degree \text{C} \quad \text{(R5)}
\]

These reactions occurred spontaneously at the temperature ranges described, which corresponded to temperature ranges indicating ΔG < 0 by FactSage (see Supplementary material and Fig. S3), and depended on the thermophysical properties of NH₄Cl. Minor products (i.e., NH₂OH·HCl) may be generated via similar thermal reactions. Based on these findings, we suggest that chlorination of the carbon matrix was blocked because Cl derived from copper was preferentially consumed by ammonium. The spectral shape of the Cl K-edge showed the small pre-edge, and the peak shape changed at 300 °C (Fig. 4A). Ratios of the chlorine chemical forms were 44% CuCl, 25% NH₄Cl, and 31% aromatic-Cls, as shown in Fig. 4B. The intensity of the raw CI K-edge spectrum decreased dramatically from 200 to 300 °C (Fig. 4C), indicative of decreasing chlorine concentrations in the solid phase [43,44]. Since forms of chlorine in the solid phase were NH₄Cl and NH₂OH·HCl at 200 °C, gasification of these compounds occurred as temperatures increased from 200 to 300 °C. CuCl and aromatic-Cls were interpreted as residual small components in the solid phase. The spectral shape changed slightly at 400 °C compared with 300 °C. NH₄Cl vanished completely in the solid phase (Fig. 4B), and the chlorine content in the solid phase decreased further because of decreasing Cu K-edge intensity (Fig. 4C). Thus, sublimation decomposition of NH₄Cl progressed gradually at temperatures from 200 to 400 °C, consistent with previous thermogravimetry data on thiourea [45].

The bonding state of sulfur was determined based on analysis of S K-edge NEXAFS. The spectral shapes at rt and 200 °C were similar to thiourea (Fig. 5), suggesting that sulfur combined with thiourea at rt–200 °C, although Copper sulfides were generated at 200 °C (ref. Fig. 3B). The molar ratio of sulfur in MFA-T(X) was sufficient to react stoichiometrically with copper. If all copper reacted with sulfur based on Cu K-edge results, the molar number of unreacted sulfur was three times higher than that of reacted sulfur. Based on this result, unreacted sulfur mainly remained in thiourea or a similar compound after isomeric reaction R1. Dynamic changes in spectral shape occurred at 300 °C. Thermal decomposition of thiourea progressed at temperatures above 246 °C, and trithiocyanuric acid (C₃H₄N₃S₃) can appear at temperatures ~220 °C [16]. In addition, FT-IR results showed representative bands of thiourea [46] (see Supplementary material), which were absent at temperatures above 300 °C (Fig. S4). Thus, no thiourea was present in the solid phase at 300 °C. The S K-edge spectrum was caused by specific S-containing compounds, excluding thiourea. Specific peaks at 2480 eV were derived from characteristics of SO₄²⁻, which was sup-

**Fig. 4.** CI K-edge NEXAFS spectra of MFA-T(X) at each temperature. A. CI K-edge NEXAFS. Solid and dashed lines are experimental and reference data, respectively. rt, room temperature. B. Ratio of chlorine chemical forms. C. Raw spectra of CI K-edge NEXAFS. R values were 0.043–0.085.
reported by previous studies on the measurement of CuSO₄ [28], as shown in Fig. 5. Reference CuS spectrum showed the same peak at 2480 eV, indicating that oxidation of CuS to CuSO₄ progressed during our measurements [28,47]. CuS showed characteristic peaks at −2470 eV, which was reported using an ultradry CuS sample [28,48]. Thus, the 2470-eV peak was indicative of the S–Cu bonding state in CuS (shaded zone in Fig. 5). These characteristic peaks at 2480 eV and 2470 eV increased at increasing temperatures from 200 to 400 °C and 200–300 °C, respectively. Based on these results, sulfate and sulfide of copper increased thermally in the solid phase, which was consistent with the analytical results for copper (ref. Fig. 3). In addition, S K-edge NEXAFS revealed the bonding state of sulfur with the carbon matrix by focusing on the fingerprint region from 2469 to 2474 eV. After thermal decomposition of thiourea, specific interactions between sulfur and carbon were identified at 300 and 400 °C based on previous reports [29,30]. The bonding state of RSSR represented at 2469.9 eV was observed at 300 °C. The spectral structure at 400 °C in the fingerprint region may be derived from two peaks derived from RSR or RSH at 2470.8–2470.9 eV and RSOR at 2473.5 eV. Based on these results, the carbon matrix interacted with sulfur, and the C–S bonding state generated after thermal decomposition of thiourea at 246 °C [16]. Partial sulfidation of carbon could inhibit aromatic–Cl formation by transforming the carbon frame. The C K-edge also supported the partial sulfidization of carbon, as described below (ref. Fig. 7).

N K-edge NEXAFS spectra reflected the thermochemical interaction of nitrogen with other elements. An acute pre-edge at 400.8 eV and whole spectral shapes in MFA-T(X) at rt were similar to thiourea (Fig. 6). At 200 °C, the pre-edge peak derived from thiourea decreased its relative intensity but remained in the N K-edge spectrum. The characteristic peak at 405.3 eV increased compared with that at rt. Thus, N-bonding decreased in thiourea and increased in NH₄Cl. A lower pre-edge at 399.7 eV was also found at 200 °C. These results were suggestive of the generation of a C–N bonding state because the pre-edge from 397 to 401 eV may be caused by an imine (−N=) or amine/imine (AI) complex (−NH₂/−NH−/−N< and −N=) which were reported in previous study of NEXAFS measurements [35]. Complete thermal decomposition of thiourea in MFA-T(X) at 200–300 °C was confirmed based on S K-edge NEXAFS (Fig. 5) and FT-IR measurement (Supporting discussion and Fig. S4). Based on these results, the N K-edge spectrum over 300 °C was not reflected by nitrogen bonding with thiourea. Spectral broad peaks at 407–409 eV and 300–400 °C showed a higher energy position than that at rt–200 °C (Fig. 6). These higher broad peaks may be derived from the 1s → σ* C–N state transition [33,34]. In addition, the spectra at 300–400 °C had a pre-edge at −400 eV. This energy area was reported as representative of the 1s → π* transition, or imine or Al complex [33–35]. Spectral shapes at 300–400 °C were not similar to the original AC, suggesting that nitrogen interacted thermally with carbon after the decomposition of thiourea. Substitution of specific elements in PCDD/Fs by nitrogen may be a urea-inhibiting mechanism [13,14]. N K-edge NEXAFS supported such inhibition mechanisms, which were also caused by thiourea.

We performed measurement and analysis of the C K-edge NEXAFS spectrum. Since MFA-T(X) contained two carbon sources, such as AC and thiourea, the spectral shape at rt revealed each characteristic feature, as shown in Fig. 7. The peak at ∼285 eV maintained its
intensity and stable conditions at increasing temperatures. Thus, this peak may be caused from the $1s \rightarrow \pi^* \text{C}=\text{C}$ transition of AC [36,37]. Similarly, the post-edge structure over 291 eV may be derived mainly from the $1s \rightarrow \pi^* \text{C} \text{=} \text{C}$ transition of AC. Most characteristic areas between the $\pi^*$ and $\sigma^*$ features changed dynamically during thermal treatment. Resonances of this energy area can be assigned to functional groups that bond with basal planes and edges of the carbon matrix [34]. This area was not found in the C K-edge NEXAFS of AC and was thus a characteristic feature caused by the addition of thiourea. Other analytical results revealed the existence of thiourea at rt–200 °C. In this temperature range, the specific peak at 287.5 eV of the C K-edge was thought to be caused by the $1s \rightarrow \pi^* \text{C} \text{=} \text{S}$ resonance of thiourea. After thermal decomposition of thiourea (ref. Supporting discussion and Fig. S4), the specific peak remained in the C K-edge at 300–400 °C, which implied that sulfur, nitrogen, and oxygen thermally interacted with the carbon matrix, as described previously [34,36–39]. Sulfidizing and nitrating of carbon were consistent with the analytical results of S K-edge and N K-edge NEXAFS, respectively. Therefore, the inhibition path may have been the result of the carbon frame or edge of aromatic-Cls being exchanged by sulfur and nitrogen.

3.3. Inhibition mechanism by thiourea

The inhibition path via sulfidization of the copper catalyst was supported by GC–MS results using MFAs, Cu K-edge XANES, and S K-edge NEXAFS. The thiourea-addition model (MFA-T) showed the same concentration levels and lower distribution patterns of PCDD/Fs, PCBs, and CBzs as the no copper catalyst (MFA-B). This condition indicated deactivation of the copper catalyst by thiourea. Sulfidization of copper and the generation of CuS, Cu$_2$S, and CuSO$_4$ over 200–300 °C were identified based on spectral analyses of Cu K-edge XANES and S K-edge NEXAFS. S-containing products such as CS$_2$(g) and HNCS(g) from the thermal decomposition of thiourea at $\sim$200 °C may influence sulfidization of the copper catalyst; this mechanism prevents the catalytic behaviors of copper to generate aromatic-Cls [24,49]. Sulfur dioxide, SO$_2$(g), was reported to react with CuCl$_2$ and then CuSO$_4$ formed thermochemically [41]. So, S-containing compounds might have common sulfidization mechanisms of copper chloride. However, especially, CuS had potential to promote thermochemical formation of aromatic-Cls in solid phase [27].

Analytical results of Cl and N K-edge NEXAFS were suggestive of blocking carbon chlorination. The majority of chlorine reacted with nitrogen, after which NH$_4$Cl(s) was generated at 200–300 °C after reactions (R4) and (R5). Minor parts of chlorine was also present as NH$_2$OH·HCl(s). In addition, sublimation decomposition or gasification of these compounds occurred at 200–300 °C. Therefore, carbon chlorination was blocked by the preferential reaction of chlorine with N-containing compounds, such as NH$_2$(g) derived from the thermal decomposition of thiourea.

Thermal interactions of the carbon matrix with sulfur and nitrogen were found based on spectral NEXAFS analyses of C, S, and N K-edges. GC–MS measurements of RFAs were indicative of the dechlorination/decomposition of aromatic-Cls. Characterization of the S K-edge implied that C=S bonding states such as RSSR, RSR or RSSH, and RSOR were generated [29,30]. Spectral features of the N K-edge were indicative of the C=N bond, or imine (–$\equiv$N-) or amine/imine complex (–NH$_2$/–NH=–N< and –$\equiv$N) [33–35]. The fingerprint region between 285 and 291 eV of the C K-edge suggested that carbonbonded thermally with sulfur and nitrogen [34,36–39]. These interactions among C, S, and N progressed after the thermal decomposition of thiourea (at 246 °C) [16]. Based on these results, attacking the carbon matrix stochastically promotes exchange of the carbon frame or edge of aromatic-Cls by sulfur and nitrogen elements and specific compounds. It is noted that sulfur and nitrogen analogs of dioxins compounds have the potential to generate by addition of thiourea [50,51].

4. Conclusions

Combining the quantitative and multielement characterization results, we characterized several inhibition paths by thiourea. This multielement research method allowed us to identify the states of chemicals through an element-complementary viewpoint. Based on our experimental findings, three inhibition paths were proposed empirically: (a) Sulfidization of the copper catalyst, (b) blocking chlorination of carbon via the reaction of chlorine with N-containing compounds, and (c) changing the carbon frame involved in the attack of the carbon matrix by sulfur and nitrogen. In the future, these experimental findings will be testified by theoretical calculation based on quantum chemistry and then we will need to determine exact mechanism of thiourea.

Thiourea played a role as a donor of sulfur and nitrogen to perform multiple and synergistic inhibition of aromatic-Cls. The thermochemical roles of nitrogen from the decomposition of thiourea to the inhibition of aromatic-Cl formation were consistent with the proposed inhibition paths of urea [10–14]. Moreover, our results are suggestive of similar inhibition mechanisms by other N/S-containing inhibitors [6,7]. Thermal properties and chemical structures of N/S-containing compounds influence the decomposition of N/S-containing products. Therefore, identifying optimal N/S-containing inhibitors will contribute to the development of valuable inhibition techniques. In addition, we mainly focused on inhibition effect of thiourea for formation of aromatic-Cls when catalyzed by copper chloride in the present study. Although application of thiourea to the RFA resulted in inhibition effect, various parameters existed in real system. So, further experimental investigation will be needed to clarify the inhibition effect and mechanism of N/S-containing agents.

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Appendix A. Supplementary data

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References


