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Synergy of Iron and Copper Oxides in the Catalytic Formation of PCDD/Fs from 2-Monochlorophenol

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Abstract

Transition metal oxides present in waste incineration systems have the ability to catalyze the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) through surface reactions involving organic dioxin precursors. However, studies have concentrated on the catalytic effects of individual transition metal oxides, while the complex elemental composition of fly ash introduces the possibility of synergistic or inhibiting effects between multiple, catalytically active components. In this study, we have tested fly ash surrogates containing different ratios (by weight) of iron (III) oxide and copper (II) oxide. Such Fe₂O₃/CuO mixed-oxide surrogates (in the Fe:Cu ratio of 1.8, 0.44, and 0.11) were used to study the cooperative effects between two transition metals that are present in high concentrations in most combustion systems and are known to individually catalyze the formation of PCDD/Fs. The presence of both iron and copper oxides increased the oxidative power of the fly ash surrogates in oxygen rich conditions and led to extremely high PCDD/F yields under pyrolytic conditions (up to >5% yield) from 2-monochlorophenol precursor. PCDD/F congener profiles from the mixed oxide samples are similar to results obtained from only CuO, however the total PCDD/F yield increases with increasing Fe₂O₃ content. Careful analysis of the reaction products and changes to the oxidation states of active metals indicate the CuO surface sites are centers for reaction while the Fe₂O₃ is affecting the bonds in CuO and increasing the ability of copper centers to form surface-bound radicals that are precursors to PCDD/Fs.

Keywords

PCDD/F; dioxin; 2-monochlorophenol; iron and copper oxides; incineration; fly ashes

Introduction

The vast majority of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the environment originate from anthropogenic sources^{1–4}. The primary origin of PCDD/Fs can

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Notes

The authors declare no competing financial interest.

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be traced to the condensation of halogenated aromatics over catalytic surfaces, particularly metal-rich fly ash, in the cool zone of incineration systems.

PCDD/Fs can be formed by way of three primary pathways: *de novo* formation from carbonaceous deposits assisted by metal chlorides, gas-phase formation involving organic precursors, and surface-mediated reactions between gas-phase organic precursors and metal oxides. The latter process occurs in the cool zone of an incinerator, where the temperature falls between 200–600°C.^{5–8} These surface-mediated reactions are responsible for up to 70% of all combustion-generated PCDD/Fs.^{9–10}

A mechanism was proposed and validated, in which transition metal oxides present on the effluent particulates from high temperature zones form and stabilize surface-bound organic radicals.^{11–13} This mechanism yields pollutant-particle systems that have been termed environmentally persistent free radicals (EPFRs). EPFRs are very stable and have lifetimes of hours or days under ambient conditions. EPFRs associated with a metal oxide substrate are precursors to PCDD/Fs as they react to form dioxins by following two alternative mechanisms: (1) the Langmuir-Hinshelwood mechanism, in which two adjacent surface-bound EPFRs undergo surface condensation or (2) the Eley-Rideal mechanism in which a surface-bound EPFR reacts with a gas-phase precursor molecule.^{10, 14–16}

To fully understand the mechanism and yields of PCDD/Fs on the surface of fly ashes, model fly ash surrogates have been investigated. Surrogates containing either iron or copper oxide impregnated onto a silica matrix have been studied extensively and these transition metal oxides were found to contribute to PCDD/F formation^{10, 17–21}. The initial focus on iron and copper oxide was due to their relatively high concentrations in fly ashes and their known redox properties.^{21–24} It was found that while copper tends to be more catalytically active than iron, iron is typically present in fly ash in much higher concentrations than copper. Both Fe₂O₃ and CuO have been shown to form phenoxy-type EPFRs as intermediates in the formation of PCDD/Fs.^{25–26} These fly ash surrogates were appropriate tools to formulate a reaction mechanism as they are uniform in their composition and their chemical makeup is easily reproducible, as opposed to fly ash, whose metal content varies significantly depending on its source. Mixed oxide catalysis between iron and copper has displayed synergistic effects in a variety of applications,^{27–31} however, it has never been tested in the surface-mediated precursor pathway of PCDD/F formation. Recent study by Liao et al. found no synergy of copper chloride and iron oxide in *de novo* PCDD/F formation.³² The use of primarily single-oxide surrogates in PCDD/F formation studies discounts the presence of synergistic effects between various components in real world fly ash. To study the cooperative effects of mixed oxide catalysts on PCDD/F formation could lead to our better understanding of the roles that various metals play for the formation of PCDD/F in real fly ash.

This work focused on Fe₂O₃ and CuO co-impregnated onto silica powder to simulate the structure of combustion-generated fly ash and analyze the potential synergy between two metals in PCDD/F formation. Previous research involved single oxide fly ash surrogates containing 5% (w/w) of either Fe₂O₃ or CuO^{14, 17}. For the sake of comparison, three mixed oxide surrogates were made with a total metal oxide content of 5% (w/w) and varying ratios

of co-impregnated Fe₂O₃ and CuO. The three mixed oxide surrogates contained Fe₂O₃: CuO ratios (by weight) of 4, 1, and 0.25, which corresponds to Fe:Cu ratios (by weight) of 3.5, 0.9, and 0.2, respectively. The molar ratios of Fe:Cu are 4,1 and 0.25 respectively.

Experimental

Fly ash surrogate Synthesis

Incipient wetness method was used to prepare the mixed oxide fly ash surrogates. An aqueous solution of copper (II) nitrate and iron (III) nitrate was introduced into silica gel powder (Aldrich, grade 923, 100–200 mesh size) in the appropriate amount for incipient wetness to occur. Various ratios of Fe³⁺/Cu²⁺ were used to produce 1% Fe₂O₃/4% CuO, 2.5% Fe₂O₃/2.5% CuO and 4% Fe₂O₃/1% CuO on silica (by weight). The samples were rotated on Rotavap for 24 h at room temperature, dried 12 h at 120°C, and calcined in air for 7 h at 450°C.

PCDD/F formation reaction

The System for Thermal Diagnostic Studies (STDS) was used to investigate the surface-mediated reactions of 2-monochlorophenol (2-MCP), which is a known PCDD/F precursor⁷, over a Fe₂O₃/CuO/Silica surface. Detailed description of the system can be found in ref.³³ Briefly, a thermal reactor (4.0 mm i.d. fused silica reactor) is set in a high-temperature furnace housed within an isothermal oven that facilitates precise temperature control over all transfer lines to and from the reactor (180 °C). A GC-MS system is interfaced in-line with the thermal reactor for analysis of combustion products.

A small amount of mixed oxide catalyst (40 mg) was placed between quartz wool plugs in the thermal reactor. To avoid condensation of the reaction products, all transfer lines were maintained at a constant temperature of 180 °C. Prior to each experiment, the mixed oxide catalyst was oxidized in situ at 450 °C for 1 h under an air flow of 5 cc/min to oxidize the surface of the fly ash surrogate. 2-MCP (Aldrich, 99%) was introduced into the flow stream by a digital syringe pump (KD Scientific, model-100) through a GC injection port maintained at 185 °C. Two carrier gases were used: air (~21% O₂) for oxidation experiments and pure nitrogen for pyrolytic experiments. The rate of injection was set to maintain a constant gas phase concentration of 50 ppm of 2-MCP with a residence time of 0.2 s. Reaction temperatures range from 200 to 550 °C. In between runs the transfer lines were baked out at 210 °C in air flow and blank run was performed to check for trace residue of products. The reaction time at each temperature is 75 min and at the same time products were collected. For the studies at each temperature, a fresh batch of fly ash was used.

The products from the reaction were analyzed using an in-line Varian CP-3800 GC system. A 30 m, 0.25 mm i.d., 0.25 μm film thickness column was used (HP-5MS) for product separation. The temperature was held at –60 °C for the reaction period followed by a ramp from –60 to 300 at a rate of 10 °C min⁻¹. Detection and quantification of the products were obtained on a Varian Saturn 2000 mass spectrometer, which was operated in full-scan mode from 15 to 450 amu for the duration of the GC run. Identification of the eluting compounds was done based on the mass spectrum of the eluent and the retention time comparison to a

standard. The amount of the formed products was calculated based on the calibration curves using respective standard solutions. The following standards were used for the calibration of PCDD/F products based on the peak area in the chromatogram: dibenzofuran (DF), 2-chlorodibenzo-*p*-dioxin (MCDD), 4-chlorodibenzofuran (MCDF), 2,7-/2,8-dichlorodibenzo-*p*-dioxin (DCDD). For the selected PCDD/F compounds, calibration was based on the MS response to the similar compounds: The calibration curve for DCDD was used to calculate DCDF, trichlorodibenzo-*p*-dioxin (TriCDD) and tetrachlorodibenzo-*p*-dioxin (TetraCDD). The yields of the products were calculated by use of the expression:

$$Y = \frac{[PROD] \times A}{[2-MCP]_0} \times 100 \% \quad [1]$$

where [PROD] is the concentration of specific product formed (in moles), [2-MCP]₀ is the initial concentration of 2-MCP (in moles), and A is the molar stoichiometric factor. Quantitative standards were used to calibrate the MS response for all products. Total yield of the PCDD/F for each temperature is defined as:

$$Y_T = \sum Y_{PROD} \quad [2]$$

where PROD is: DD, DF, MCDD, MCDF, DCDD, DCDF, TriCDD, and TetraCDD. PCDD/F ratio was calculated based on the average integrated yields of PCDD and PCDF (average of the total PCDD or PCDF yields within the entire temperature range 200–550 °C). We cannot exclude the formation of higher chlorinated PCDD/F due to the chlorination reaction or condensation of higher chlorinated products, however if such reaction took place, the amount of higher chlorinated PCDD/Fs were below the instrumental detection limit. The unreacted 2-MCP is collected at the same time as PCDD/F products. The amount of detected 2-MCP is based on the 2-MCP peak area and is compared to the 2-MCP standard curve. All experimental data represent an average of three or more runs. Between each experiment a reactant/product transport analysis was performed to ensure the system was free of leaks and properly insulated.

Surrogate Fly Ash Characterization

To evaluate the oxidation state and coordination of the active metal centers of surrogate samples, X-ray Photoelectron Spectroscopy (XPS) measurements were carried out using a Kratos Axis-165 Auger/XPS system. A survey scan and high-resolution individual elemental scans were performed on the surrogate surface of each mixed oxide catalyst with the mono Al x-ray source at a beam current of 15mA and anode high tension of 15KV.

All survey scans were performed at binding energy range of 0–1200 eV with pass energy of 160 eV; High-resolution scans of all the elements were performed with pass energy of 40 eV. Composition quantification results were based on the high-resolution elemental scans before and after PCDD/F formation reactions.

EPFR formation and analysis

We studied EPFRs formation by exposing $\text{Fe}_2\text{O}_3/\text{SiO}_2$ particles to 2-MCP precursor vapors. Before 2-MCP's exposure, the particles were heated in situ at 450 °C for 1 h to remove organics on the surface. After that, these particles were exposed to the 2-MCP vapors at 230 °C in a customized vacuum exposure chamber for 6 min under vapor. After exposure, samples stayed under vacuum for 1 h to remove excess non-chemisorbed adsorbate at 10^{-2} Torr. Still under vacuum conditions, the dosed particles were cooled to room temperature before electron paramagnetic resonance (EPR) spectra were recorded. EPR spectra were recorded in a Suprasil EPR tube at room temperature using a computer-controlled Bruker EMX 10/2.7 EPR spectrometer. Instrument parameters were as follows: center field, 3470 G; sweep width, 100 G; microwave frequency, 9.7 GHz; microwave power, 2.0 mW; modulation frequency, 4.0 G; modulation amplitude, 4.0 G; receiver gain, 3.54×10^4 ; time constant, 41.0 ms; and three scans. Radical concentration was calculated using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard due to the similarity between the spectral profiles of DPPH and the radicals formed on $\text{Fe}_2\text{O}_3/\text{silica}$.

Results and Discussion

Precursor Degradation

The conversion of 2-MCP over the three-studied mixed oxide $\text{Fe}_2\text{O}_3/\text{CuO}$ surrogates is shown in Figure 1. For reference^{14, 17}, previously obtained results from single oxide surrogates are also included in the figure. Under oxidative conditions, clear differences can be observed between the mixed oxide systems and single oxide catalysts in the catalytic oxidation of 2-MCP (see Figure 1a). All three mixed oxide surrogates convert > 99.5% of the 2-MCP precursor across the entire measured temperature range (see Figure 1a). On the contrary, single oxide systems gradually increase their activity in the oxidation process in the temperature range of 200–400 °C and level-off above 400 °C. In pyrolytic conditions, mixed oxide systems are also superior to single oxides in degradation of 2-MCP, though differences are less dramatic (Figure 1b). The differences in the oxidative and pyrolytic degradation profiles indicates that 2-MCP is undergoing the Mars-Van Krevelen Mechanism.³⁴ Current experiments further confirm this theory, where in the absence of molecular oxygen, oxidation of 2-MCP still occurs. Higher activity of the mixed oxide systems at lower temperatures (below 400 °C) indicates a more energetically favorable abstraction of oxygen from the surface by the adsorbed molecules in mixed oxide samples compared to single oxides. This higher activity supports the hypothesis that synergy between iron and copper oxides is primarily due to weakened metal-oxygen bonds. Previous studies³⁵ have indicated that the adsorption of aromatic species on metal oxides leads to the formation of surface radicals and the mechanism for EPFR formation on individual transition metal oxides has been thoroughly characterized.^{11, 17} Depending on the reactivity of the system and the reaction temperature, this leads to degradation/oxidation products or condensation of such radicals to form larger species (such as PCDD/Fs and others). The surface-mediated precursor mechanism for PCDD/F formation can also be applied to mixed oxides. Indeed, the exposure of mixed metal oxide systems to the vapors of 2-MCP at 230°C have shown the formation of EPFRs, similarly as described for the single metal systems.²⁶ These radicals are identified as a mixture of phenoxy- and semiquinone-type radicals (cf. Figure 1S, Table

1S in Supporting Information). The EPR spectra in Figure 1S indicate the formation of free radicals over three fly ash surrogates, respectively. The concentration of EPFRs presented in Table 1S are 2.5%Fe₂O₃/2.5%CuO > 4%Fe₂O₃/1%CuO > 1% Fe₂O₃/4%CuO. The analysis of the radical speciation is typically done by the linear combination and peak fitting of the collected spectra. The detected spectra are very similar to the one observed before for CuO systems described earlier¹⁰. By inference we have concluded that same radical species are present in the mixed metal oxide samples.

PCDD/F Formation

Under oxidative conditions, the yields of PCDD/Fs are very small (Supporting information, Figure 2S). Surface-formed radicals are subject either to condensation process or further oxidation to smaller molecules and CO₂. There is a competition between the oxidation and condensation processes and under oxygen-rich conditions the rate of destruction of 2-MCP surpasses the rate of condensation of PCDD/F intermediates as indicated by almost complete destruction of 2-MCP. In the absence of molecular oxygen, the rate of catalytic oxidation of 2-MCP is suppressed and the rate of condensation of surface species increases yielding formation of PCDD/Fs (Figure 2). In fact, PCDD/F yields on the mixed oxide catalysts under pyrolytic conditions are up to five times higher than any previously measured yield from a single oxide catalyst. This applies particularly to the mixed oxide samples containing 2.5% of CuO and less (Fe:Cu ratios 0.88 and 0.4). The samples containing 1% Fe₂O₃ still formed higher yields of PCDD/Fs than either single oxide samples, however much less than the other two studied mixed oxide catalysts.

Total PCDD/F yield and corresponding standard deviation data for pyrolysis is included in Table 2S in supporting information. All the dioxin and non-dioxin products for both oxidation and pyrolytic conditions are also included in supporting information from Table 3S–Table 8S.

Mixed oxide systems have shown a clear temperature shift in the PCDD/F formation window under pyrolytic conditions. While for the single oxides, formation of PCDD/Fs started above 300 °C (for Fe) and 350 °C (for Cu), mixed oxide systems have shown formation of PCDD/Fs already at 200 °C with a clear maximum at ~ 275–300 °C. A correlation between the degradation of 2-MCP and the beginning of PCDD/F formation shows the point at which the surface is sufficiently activated to form surface-bound intermediates. Comparing the onset of the PCDD/Fs formation temperature with the 2-MCP degradation profiles, it appears that ~93–94% degradation of MCP marks the activity threshold for the PCDD/F formation onset (with the exception of Fe:Cu = 1:1 at 200 °C, where 2-MCP degradation is at 86%).

We have shown previously a significant difference in the PCDD and PCDF yields for copper and iron oxides from 2-MCP^{14, 17}: copper oxides preferentially formed PCDDs, while iron oxide formed primarily PCDFs. By using 2-MCP in current studies we were hoping to identify which metal center dominates the PCDD/F formation process in mixed oxide systems. PCDD:PCDF ratios for all samples are shown in Figure 3. The congener profiles of all three mixed oxide systems contain higher quantities of PCDDs across the entire studied temperature range. Even the PCDD:PCDF ratio of the 4% Fe₂O₃/1%CuO surrogate is much

closer to that of the 5% CuO surrogate. The mechanistic reason for the increased PCDD/F yield for samples containing less copper or “diluted” by iron oxides is at present not known. It might be associated with the electronic effects of iron oxide presence and potential stabilization of the surface radicals. PCDDs are formed through Eley-Rideal (E-R) reactions of surface bound EPFRs with gas phase precursors, and PCDFs are formed through the condensation of surface radicals. Surface immobilization of EPFRs prevent their lateral-movement, affecting either condensation with other surface species or subsequent surface oxidation. In fact, it is most likely the fast surface oxidation of PCDF precursors that is responsible for the smaller yields of PCDFs. For example, 4,6-dichlorodibenzofuran (DCDF) formation on the surface of mixed metal oxides reaches maximum at 300 °C (0.8% yield) for samples containing 1:1 ratio of iron and copper and quickly drops to zero with increasing temperatures (Figure 3S, supporting information). As a result, such species become more available for reaction with the gas phase precursor to form PCDDs.

Iron-Copper Interaction

The observed synergistic effects indicate a likelihood of direct contact between the Fe₂O₃ and CuO on the surface of the fly ash surrogate. Such co-location could explain the increased PCDD/F yield for samples with decreasing copper concentration – one can anticipate a dilution of surface copper sites (*vide supra*) within the iron oxide phase and increased iron-copper electronic interaction. In fact, higher activity of mixed metal systems (at the same metal load) prompts the hypothesis that synergy between iron and copper oxides affects the metal-oxygen bonds and enhanced reactivity in Mars-Van Krevelen type oxidation (as observed in this case – figure 1). Figure 4 presents a comparison of Cu 2p spectra from the catalytic samples after reaction with 2-MCP under pyrolytic conditions. Binding energy absorption peaks were fitted to different oxidation states and speciation of copper and the percent of Cu reduction from +2 to +1 oxidation state were calculated. Addition of Fe₂O₃ into the CuO samples results in gradual increase of the copper reduction. Small addition of iron (1% Fe₂O₃ + 4% CuO) already results in almost double the degree of copper reduction: 78.5% of the Cu is reduced compared to the 48.8% reduced in the pure CuO surrogate. In the 1:1 mixture of copper and iron oxides, more than 90% of copper is reduced after reaction. The increased reducibility of copper in mixed oxide systems implies an interaction between iron and copper ions and their direct contact. In such case, Iron(III)-Cu(II)O long distance interaction pushes the electron cloud towards copper resulting in an increased affinity of Cu²⁺ to accept an electron. Such effects were observed earlier for Cr(III)Cu(II) systems³⁶. Because EPFRs are formed by an electron transfer between an adsorbed species and a metal center, one can anticipate that increased affinity of Cu²⁺ ions to electrons will also accelerate the formation of EPFRs and/or increase their stabilization on the surface. No significant changes were observed within the Iron binding energy range that would indicate reduction. This supports our conclusion that copper is the primary site of EPFR formation. Since PCDD/F formation is dependent on surface coverage by EPFRs, higher concentration of longer lasting EPFRs results in higher PCDD/F yields.

The effects of Fe-Cu electronic interaction in mixed metal oxide catalysts are manifested in dibenzo-p-dioxin (DD) and monochlorodibenzo-p-dioxin (MCDD). Both DD and MCDD are formed by similar E-R mechanisms, the difference being the reaction site of gas-phase

molecule attack, either at the hydroxyl group or the chlorine of the adsorbed EPFR (Scheme 1).¹⁰ As seen in Figure 5, the single oxide and mixed oxide surrogates primarily form DD and MCDD, respectively. We infer that as the Fe-Cu interaction affects the reducibility of copper sites, the electron density of the associated Cu-adsorbate can be affected, increasing the rate of Cl abstraction/substitution by copper sites. Alternatively, since reaction at the OH site results in the stronger adsorbed species¹³, this can lead to oxidation of surface-bound DD (mixed oxide systems indicate much higher oxidative potential. cf. Figure 1). DF formation is only detected by pure iron oxide or samples with high iron content. As reported earlier, this is associated with the decomposition reaction of precursor on the surface of iron leading to the formation of phenoxy species.¹⁷ This process is slowed if copper is present.

The PCDD/PCDF ratio on iron oxide catalyst from 2-MCP precursor is generally driven by the formation of dibenzofurans, a condensation product resulting from partial degradation of bidentate adsorbate intermediate³⁷, resulting in dichlorination of the parent molecule and formation of condensation products with two less chlorine atoms. The introduction of copper oxide to the system has an inhibiting effect on DF formation, and only the highest Fe content samples indicate DF formation in reaction products (Figure 6). No DF formation upon introduction of copper results in increased PCDD/PCDF ratios.

Study Implications

It was reported that the different incineration systems can produce varying ratios of PCDDs to PCDFs, depending on the conditions within the systems. Our previous studies have shown that in some cases it is the metal speciation that can determine the PCDD to PCDF ratios. Liao et al. studied Fe₂O₃ and CuCl₂ catalysis of PCDD/F formation during de novo tests, however, no synergistic effect between iron and copper was observed³². Our current study of mixed copper-iron oxide systems has confirmed the importance of metal speciation on the PCDD/Fs ratio.

However, more important finding is the synergy effect between different metals on the overall yields of PCDD/Fs. The observed yields of PCDD/Fs are very high (up to 5% for MCDD) compared to other studies for single metal systems (fractional percentage values) for pyrolytic conditions (Table 1). On the contrary, almost no PCDD/Fs are observed at oxygen-rich conditions, where single metal oxides usually produce more PCDD/Fs.³⁷ This reverse trend is most likely a result of high oxidation power of mixed oxide systems. Since fly ashes in combustion systems are characterized by complex composition⁴², including multiple metals, their mutual interactions can be anticipated. Such interaction, as in the studied Cu-Fe system, can change entirely the dynamics of PCDD/F formation. In case of Cu-Fe interactions, our studies indicate, that pyrolytic pockets within the combustion exhaust systems would be a driving force behind increased PCDD/F emissions. This can be prevented by engineering solutions such as improvement of mixing of gasses within the exhaust to promote complete oxidation of PCDD/F precursors.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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1. Iron and copper often cohabit on particulate matter in combustion systems.
2. Under pyrolysis, synergy of iron and copper oxides produced almost 10-fold increased yields of PCDD/Fs compared to single CuO or Fe₂O₃ oxide fly ash surrogates.
3. CuO influences the PCDD/F congener profile while the presence of Fe₂O₃ affects the PCDD/F yields.

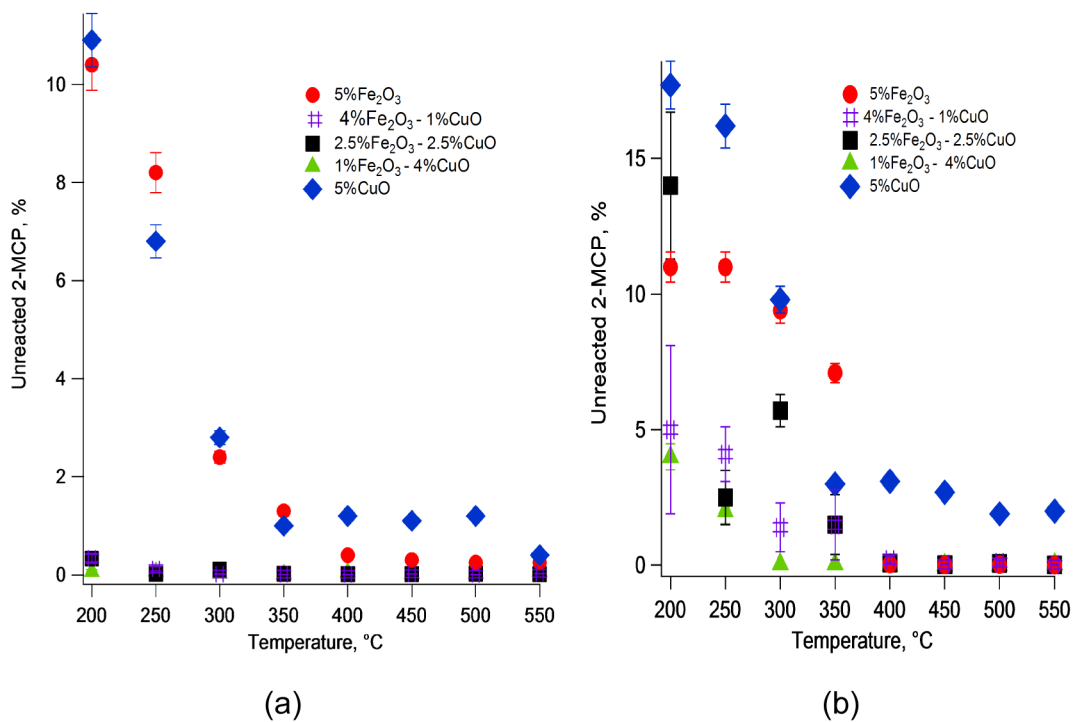


Figure 1. Catalytic degradation of 2-MCP over three mixed oxide catalysts under (a) oxidation conditions and (b) pyrolytic conditions. Single oxide catalyst data included for reference.

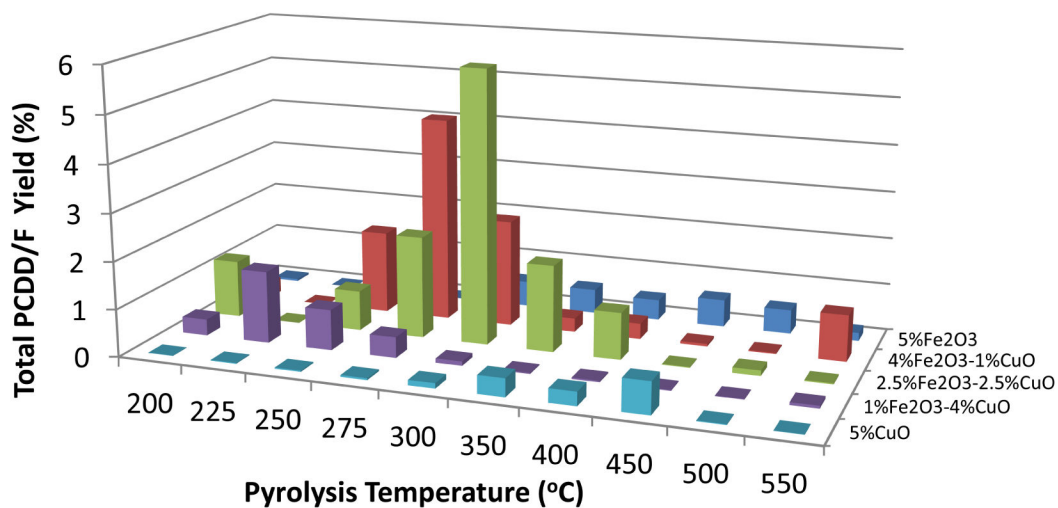


Figure 2. Total PCDD/F yields from the pyrolytic degradation of 2-MCP over Fe/Cu mixed oxide catalysts.

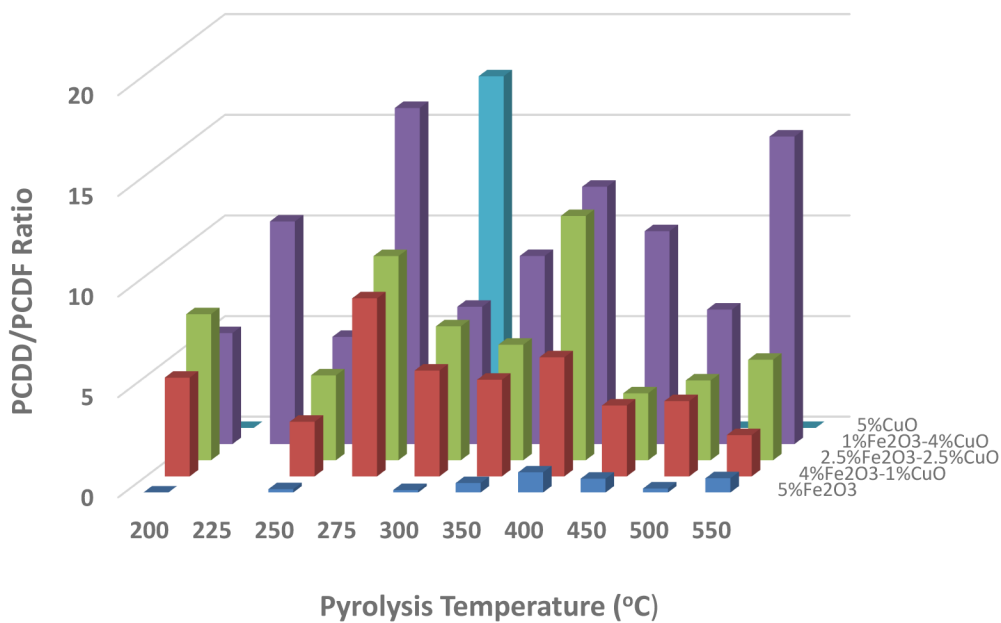


Figure 3. PCDD/PCDF ratios from the pyrolytic degradation of 2-MCP over Fe/Cu mixed oxide catalysts.

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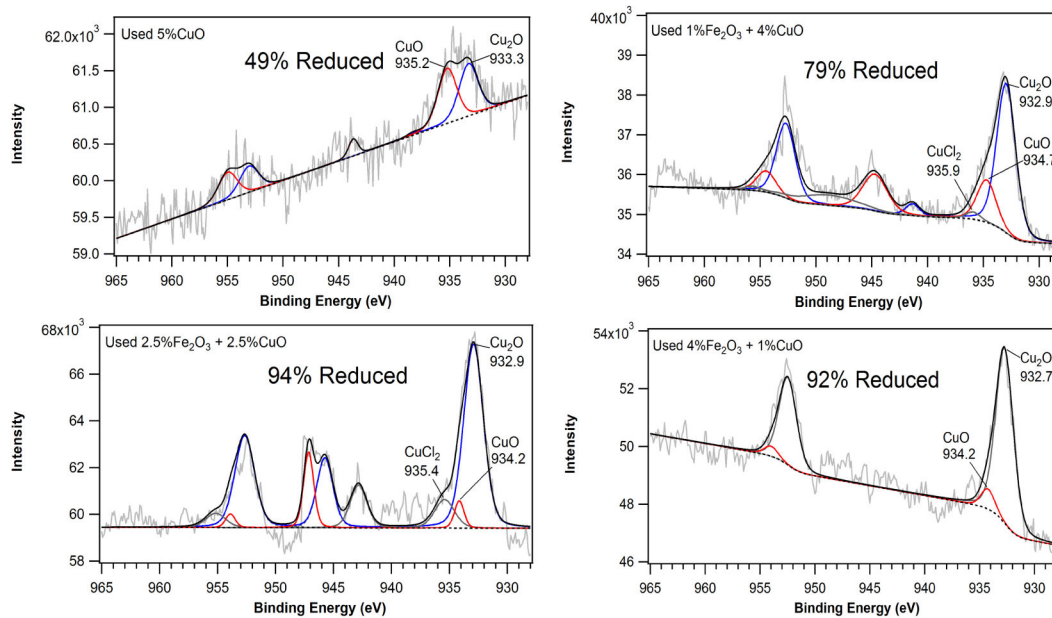


Figure 4. High Resolution XPS spectra of the Cu 2p binding energy region with fitted peaks corresponding to Cu²⁺ and its reduced forms: Cu₂O and CuCl₂. The percent of reduced copper after PCDD/F formation is emphasized for each surrogate.

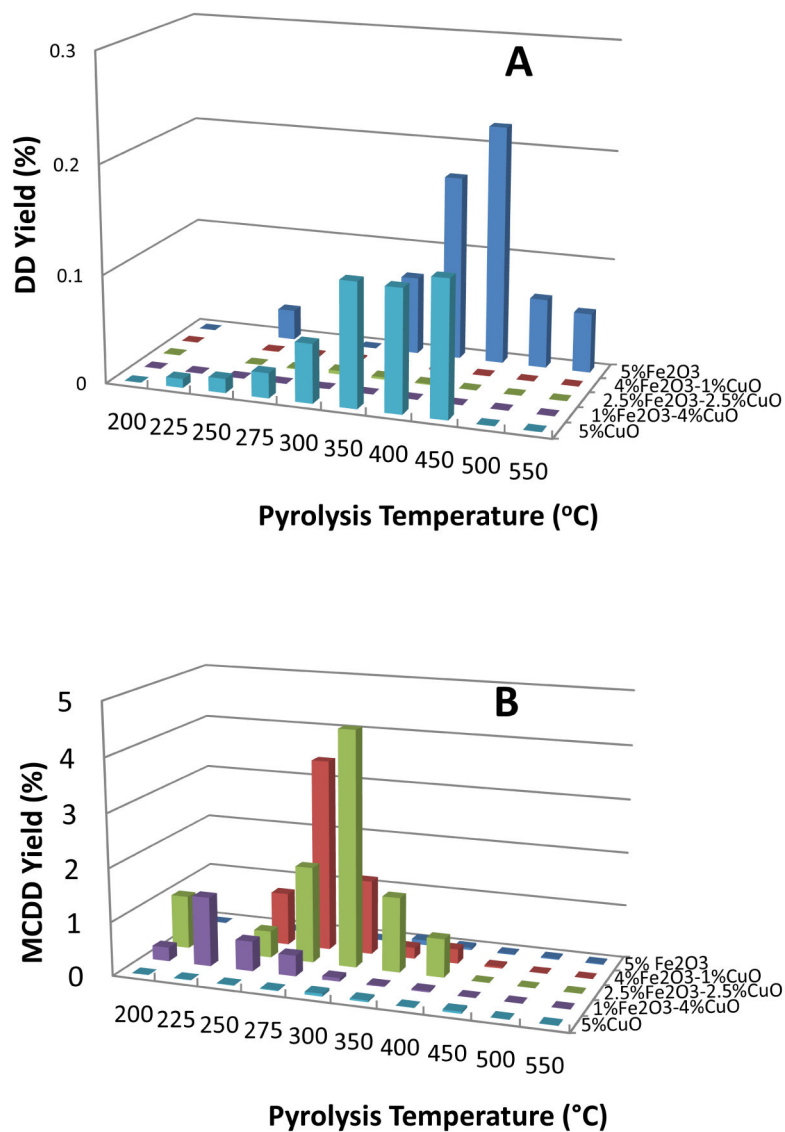


Figure 5. (A) Dibenzo-*p*-dioxin and (B) monochlorodibenzo-*p*-dioxin yields from the pyrolytic degradation of 2-MCP over Fe/Cu mixed oxide catalysts.

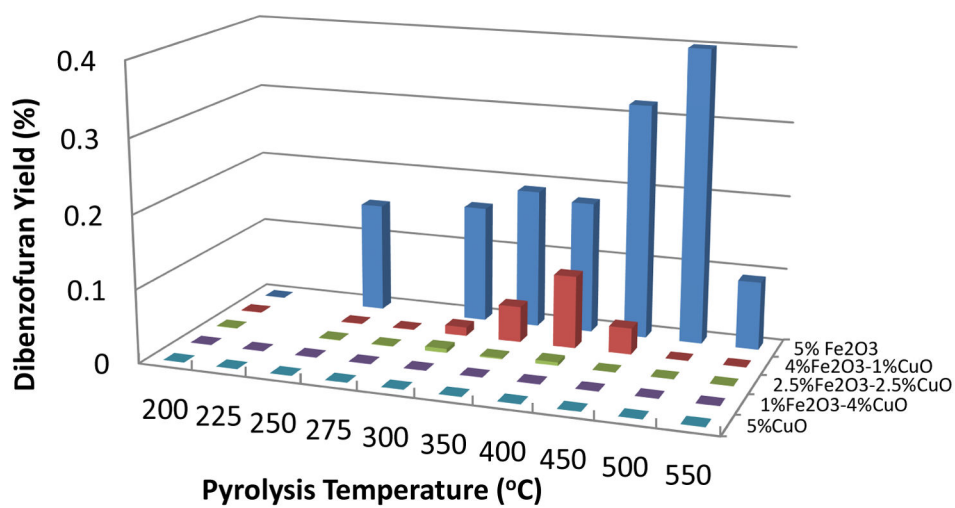
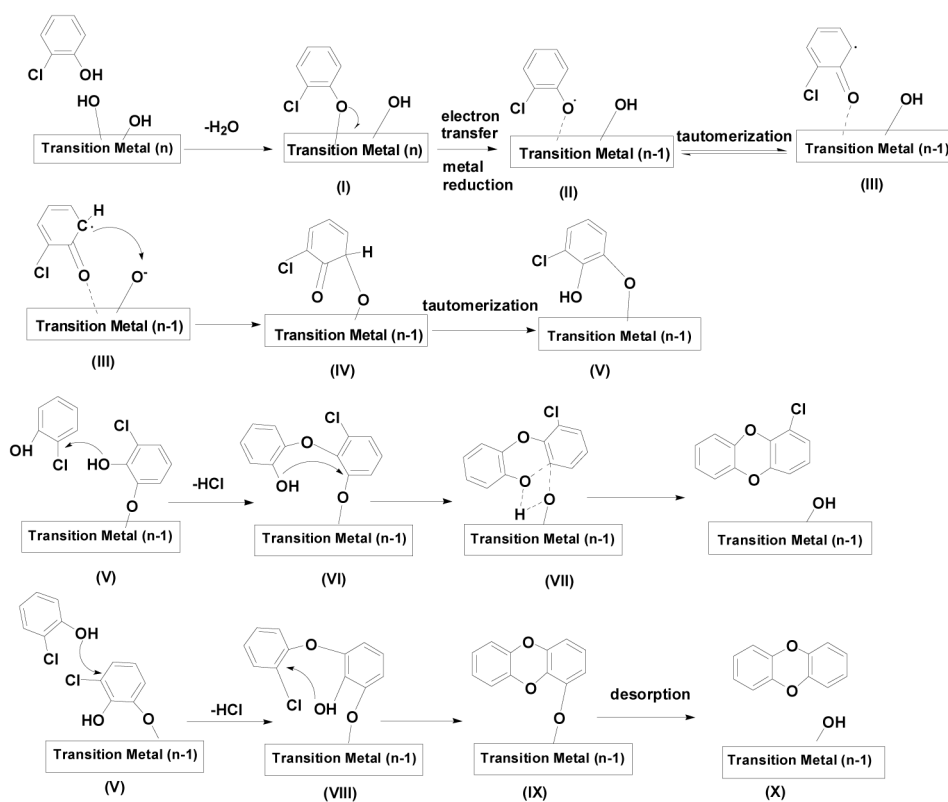


Figure 6. Dibenzofuran yields from the pyrolytic degradation of 2-MCP over Fe/Cu mixed oxide catalysts.



Scheme 1.
DD and MCDD formation mechanisms (adapted from ¹⁰)

Table 1

Maximum yields of PCDD/F for pyrolytic conditions from this study and previous studies^a

catalysts	model	PCDDs	PCDFs	PCDD/PCDF	references
CuO/Fe ₂ O ₃	precursor	7.9 %	1.3 %	6.1	This study
CuO	de novo	1.2×10 ⁻⁵ %	1.7×10 ⁻⁵ %	0.71	M. Zhang et al. 2016 ³⁸
CuCl ₂ /Fe ₂ O ₃	de novo	3.0×10 ⁻⁴ %	2.0×10 ⁻³ %	0.15	J Liao et al. 2016 ³²
CuO	precursor	0.58 %	0.68 %	0.85	S Nghanai, et al. 2014 ^{4, 6, 39}
Fe ₂ O ₃	precursor	0.31 %	0.78 %	0.40	S Nghanai. et al.2008 ^{2, 5, 17}
CuCl ₂	precursor	1.4 %	5.7 %	0.25	J Ryu et al. 2005 ⁴⁰
CuO	precursor	0.22 %	0.13 %	1.7	S Lomnicki et al.2003 ¹⁴
CuCl ₂	de novo	5.7×10 ⁻⁴ %	3.0×10 ⁻³ %	0.19	V. Pekarek et al. 2001 ^{8, 41}

^aPCDD/F yield was calculated on input of carbon.