3. Effect of other trace metal oxides on the formation of CBzs and PCBs

There are a range of metal elements in trace amounts in fly ash, such as Al, Mg, Pb, Cr, Cu, Mn, that might also influence the formation of chlorinated aromatics during iron ore sintering. In this study, 0.5 wt.% of PbO and MnO was added to the SFA to investigate the effect of trace metals on the formation of CBzs and PCBs (**Figure 3**). The production of both CBzs and PCBs decreased slightly from 1.9 ×103 ng/g-fly ash to 1.4 ×103 ng/g-fly ash for CBzs, and from 41 ng/g-fly ash to 38 ng/g-fly ash for PCBs after adding MnO to the SFA. However, the yield of CBzs increased sharply to 13,000 ng/g-fly ash, while the generated amount of PCBs showed a decrease to 23 ng/g-fly ash with PbO addition. Fujimori et al. prepared SFA with KCl, AC, PbO and SiO_2, and found that PbO had a suppressing effect on the formation of chlorinated aromatics, since PbO inhibits the oxidation of the carbon matrix and blocks the formation of CBzs[6]. However, the formation of CBzs was obviously promoted in our investigation. PbO might have a synergetic effect with CuO and/or Fe_2O_3 thereby promoting the formation of chlorinated aromatics.

4. Mechanism analysis of CBz, PCB and PCDD/F formation

The chlorinated aromatics formed in the SFA at 350 ℃ were mainly generated by *de novo* synthesis from carbon in the presence of chlorides and metal catalysts[7]. The formation mechanism of CBzs, PCBs and PCDD/Fs was deduced based on the *in situ* XPS analysis of the SFA and product analysis during thermal treatment of SFA10:1 (**Figure 4**). CuO and Fe_2O_3 were the dominant catalysts for CBz, PCB and PCDD/F formation in SFA. On one hand, they react with Cl^- to form $CuCl_2$ and $FeCl_3$, which provides further potential catalysts for *de novo* synthesis, since they serve as both catalysts and chlorine sources. The Deacon reaction was promoted in the presence of $CuCl_2$ and $FeCl_3$, and consequently more Cl_2 was produced for the chlorination of the native carbon in the SFA[8]. On the other hand, CuO and Fe_2O_3 could be reduced to Cu/Cu_2O and FeO/Fe_3O_4 in the presence of native carbon in SFA. Therefore, the oxidation and chlorination of native carbon was promoted. Native carbon in the SFA could be chlorinated and oxidized to form short-chain chlorinated hydrocarbons, such as CH_2Cl_2 and $CHCl_2$, in the presence of Cu/Fe catalysts and a chlorine source. With increasing carbon chain length, chlorinated aromatic CBzs and PCBs were formed. Finally, PCDDs and PCDFs were synthesized by hydroxyl (OH) attack on CBzs and PCBs, followed by HCl elimination.

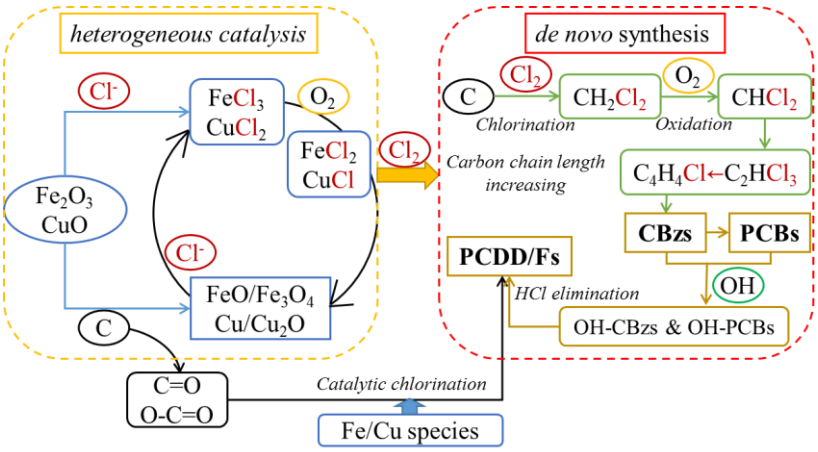

Figure 4. Formation mechanism of CBzs, PCBs and PCDD/Fs.

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