EFFECT OF SELECTED METAL OXIDES ON DECHLORINATION AND DESTRUCTION OF PCDD AND PCDF

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Introduction

In the presence of oxygen, fly ashes from waste incineration catalyze the *de novo* synthesis of PCDD/F, starting at temperatures as low as 200°C[1-3]. On the other hand, Hagenmaier et al. showed that fly ash catalyzes in the same temperature window the dechlorination/hydrogenation of chlorinated aromatic compounds[3]. The latter property of fly ashes is favorably used for the low temperature decontamination of fly ashes in industrial scale[4-6].
Copper, platinum and rhodium were found to catalyze the dechlorination/hydrogenation reaction while the other metals/metal oxide tested were assigned only a destruction potential[3, 7].
Copper compounds are, however, minor components in fly ashes ranging between 100 and 5000 ppm. Therefore it seemed interesting for us to investigate the oxides from other selected metal oxides on model fly ashes, in respect to their dechlorination and destruction potential in comparison to copper compounds.

Materials and Methods

Model fly ashes (MFA) were prepared by grinding silica with graphite (2%wt) and the respective metal oxide (5%wt with the exception of $Ca(OH)_2$ with 10%wt).
Despite the copper compounds (elemental Cu, Cu_2O, $Cu(OH)_2$), we chose as metal oxides main components in fly ashes and fly ashes resulting from melting processes (Fe_2O_3, ZnO, PbO, SnO, $Ca(OH)_2$).
The elemental analysis for impurities in the metal compounds were measured according to JIS K 0116 with the ICPS 1000-3 (Shimadzu Co. Ltd., Kyoto, Japan).
The model fly ashes (100 mg) were spiked with OCDD (500 ng/g) and the solvent evaporated at room temperature. The ashes were heated under nitrogen or argon atmosphere (oxygen exclusion) in glass ampoules sealed under atmospheric pressure.
The procedures for extraction, clean up and analysis are reported elsewhere[8,9]. MonoCDD (MCDD), diCDD (DCDD) and triCDD (T_3CDD/F) were analyzed by HRGC/LRMS on a Sil 88 or a DB5 column using a HP 6890 gas chromatograph connected to a HP 5973 mass spectrometer.

Results and Discussion

All tested copper compounds showed considerable dechlorination on the silica/graphite model fly ash system at 260°C (Figure 1). Under these testing conditions, Cu_2O exhibit the highest dechlorination rates followed by elemental copper and $Cu(OH)_2$.
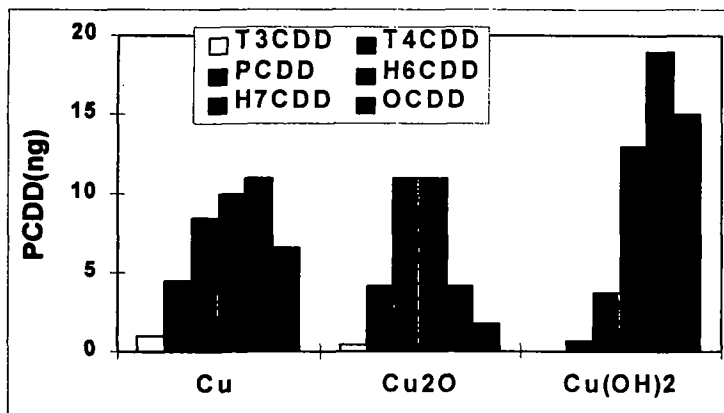
Figure 1: Dechlorination of OCDD (50 ng) on model fly ash (silica, 2% graphite) containing copper compounds (5%) under exclusion of oxygen at 260°C (30 min)

The other tested metal oxides showed considerably lower dechlorination potency at 260°C, however, all model fly ashes - even in the "blank test" on silica/graphite - resulted in at least 0.5% H_7CDD (Figure 2). From the tested compounds, Fe_2O_3 and SnO showed the highest dechlorination potential resulting in an average chlorination degree of 7.5 and 7.7 respectively.
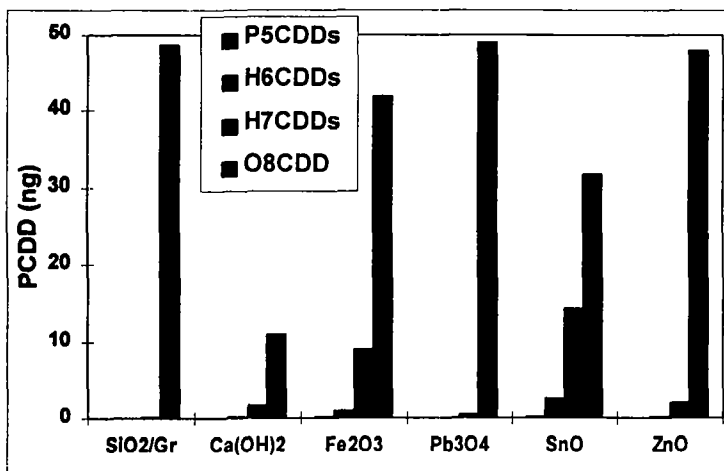
Figure 2: Dechlorination of OCDD (50 ng) on model fly ash (silica, 2% graphite) with selected metal oxides (all 5%, $Ca(OH)_2$ 10%) under exclusion of oxygen at 260°C (30 min) in comparison to the blank test on silica/graphite (SiO_2/Gr)

The OCDF was dechlorinated in all cases to a higher degree compared to OCDD. Especially the dechlorination step of the 1,9-position in OCDF - the thermodynamically most unstable position - is hydrogenated faster than the positions in OCDD. E.g. the OCDF was dechlorinated on the MFA containing SnO after 30 min at 260°C to more than 72% while OCDD was dechlorinated in the same experiment to less than 37% (Figure 3).
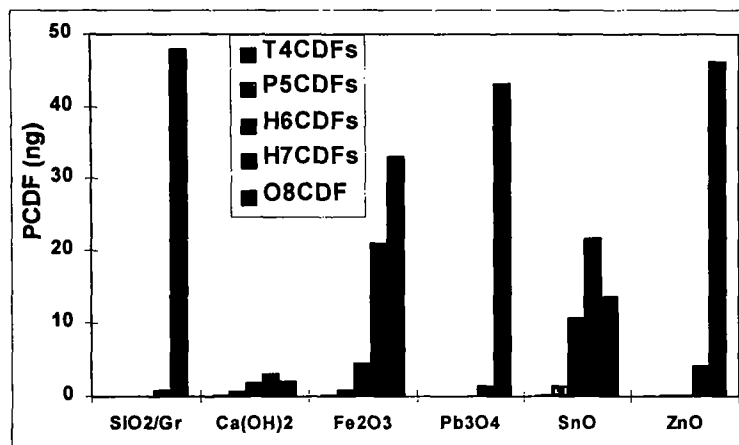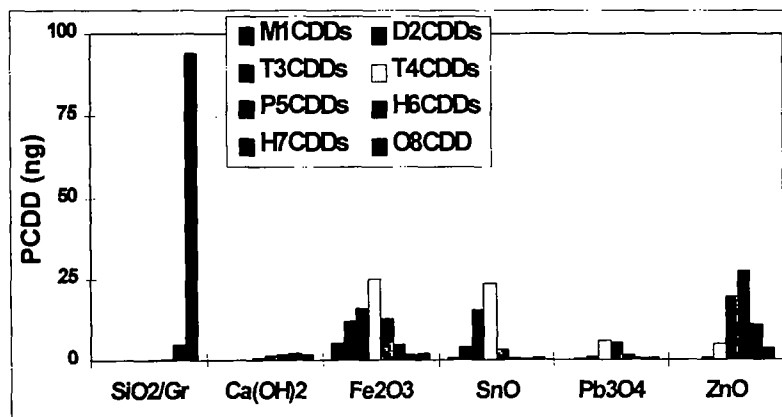
Figure 3: Dechlorination of OCDF (50 ng) on model fly ash (silica, 2% graphite) with selected metal oxides (all 5%, $Ca(OH)_2$ 10%) under exclusion of oxygen at 260°C (30 min) in comparison to the blank test on silica/graphite (SiO_2/Gr).

$Ca(OH)_2$ exhibits the highest destruction potential of the tested compounds. After 30 min at 260°C, less than 30% of OCDD and less than 20% OCDF was recovered on the model fly ash, while for all other tested compounds, the recovery was higher than 80%.

The difference in destruction rate of OCDD on fly ashes from municipal solid waste incineration with and without $Ca(OH)_2$-spray during thermal treatment we also mainly assigned to the influence of $Ca(OH)_2$ and the resulting basic matrix[10].

At 340°C with all tested copper species the dechlorination/destruction was nearly "completed" after 30 minutes. Less than 0.5 % of the spiked OCDD was recovered as T_4CDD-OCDD and less than 10% was recovered as $MCDD$-T_3CDD and dibenzo-p-dioxin. The completely hydrogenated dioxin backbone (dibenzo-p-dioxin) is, therefore, not the final main product of the thermal decomposition as was already stated by Hagenmaier et al.[7].

All the other tested metal oxides showed a considerable effect on dechlorination/hydrogenation at 340°C on the silica/graphite model fly ash which is not observed in the silica-graphite "blank test" (Figure 4). The average chlorination degree of PCDD range from 3.6 for SnO to 6.7 for $Ca(OH)_2$.

Figure 4:
Dechlorination of OCDF (100 ng) on model fly ash (silica, 2% graphite) with selected metal oxides (all 5%, $Ca(OH)_2$ 10%) under exclusion of oxygen at 340°C (30min) in comparison to the blank test on silica/graphite (SiO_2/Gr)

We performed an elemental analysis of the used metal oxides including graphite and silica, to exclude a contamination by copper impurities. All samples were below the detection limit (5 ppm) with the exception of Fe_2O_3, containing 33 ppm "Cu" impurity. In our opinion, also,

the detected amount of copper in Fe_2O_3 is too small to explain the observed dechlorination effect. Therefore most metal oxides are able to catalyze the dechlorination/hydrogenation reaction of PCDD/F.

In the dechlorination/hydrogenation reaction a chlorine atom in the PCDD/F is substituted by a hydrogen atom. The "chemistry" of this reaction is therefore a reduction where the carbon in the OCDD/F backbone changes the oxidation number* due to the substitution of Cl by H. For the "Redox" reaction, on the other hand, a oxidation of a metal (oxide) seems inevitable. However, e.g. $Cu(OH)_2$ (ZnO, Fe_2O_3) are already in their highest oxidation state. Therefore $Cu(OH)_2$ (ZnO, Fe_2O_3) are not capable of supporting a reduction. In our opinion, in the first step $Cu(OH)_2$ is partly reduced by e.g. the present carbon matrix. In the second step, the reduced copper compound (metal compound) is then able to support a reduction and the dechlorination/hydrogenation reaction.

In the case of $Ca(OH)_2$, a alkaline earthmetal with a standard reduction potential ($E°$) of -2.87 V, a dechlorination mechanism involving reduction/oxidation seems impossible. An explanation for the observed effect on dechlorination of OCDD/F are the influence of the 2000 ppm heavy metal impurities including Cr, Fe, Mg, Mn and Ti detected in the elemental analysis of the used $Ca(OH)_2$.

In this respect, further investigations are needed regarding the oxidation/reduction processes involved and the influence of metal impurities in the ppm range.

Acknowledgment

References

1. Vogg H. and Stieglitz L. (1986) Chemosphere 15, 1373.

2. Stieglitz H., Zwick G., Beck J., Roth W. and Vogg H. (1989), Chemosphere 18, 1219.

3. Hagenmaier H., Brunner H., Haag R. and Kraft M. (1987) Environ Sci. Technol. 21, 1080.

4. Stützle R., Hagenmaier H., Hasenkopf O. and G. Schetter (1991) VGB Kraftwerkstechnik 71 (11), 1038.

5. Trumpf R., Christmann A. and Hagenmaier H. (1998) UTA International 7, 82.

6. Ishida M., Shiji R., Nie P., Nakamura N. and Sakai S. (1996) Organohalogen Compounds 27, 147.

7. Hagenmaier H., Brunner H., Haag R. and Kraft M. (1987) Environ Sci. Technol. 21, 1085.

8. Takasuga T., Makino T., Tsubota K., Takeda N. Chemosphere (2000) 40, 1003.

9. Höckel J., Düsterhöft L., Körner W. and Hagenmaier H. (1995) Organohalogen Compounds 23, 139.

10. Weber R., Takasuga T., Nagai K., Shiraishi H., Matuda T. and Hiraoka M. (2000) Organohalogen compound, this volume.