

Catalytic oxidation - a technology for the reduction of PCDD/PCDF emission from waste incineration facilities to below 0.1 ng TEQ/m³

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Summary

When the possibility of the catalytic oxidation of PCDD/PCDF in the temperature range of 150 - 500°C was demonstrated, many commercially available oxidation catalysts and other catalysts on the basis of metals and metal oxides were tested. It was found that catalysts produced for the selective catalytic reduction of nitrogen oxides in the presence of ammonia (SCR-catalysts) exhibit some unexpected properties as oxidation catalysts for the decomposition of organohalogen compounds in general and of PCDD/PCDF in particular. While most recognized oxidation catalysts did not exhibit any activity below 300°C under the conditions of our laboratory experiments, SCR catalysts on the basis of TiO₂ showed under otherwise identical conditions high activity as oxidation catalysts for organochlorine compounds at temperatures of 250 - 350°C. Under appropriate conditions, organochlorine compounds could be decomposed by catalytic oxidation without PCDD/PCDF formation. In pilot plant studies at municipal waste incinerators we were able to demonstrate that catalysts originally developed for selective reduction of nitrogen oxide are capable of reducing the PCDD/PCDF emissions to levels below 0.1 ng TCDD-equivalents (TEQ) per m³. Prerequisites for this PCDD/PCDF reduction are residence times in the range of 0.3 to 0.7 seconds and (either the absence of ammonia or) ammonia concentrations of less than 10 ppm. When run in the temperature range of 250 - 350°C, these catalysts can be used either solely as oxidation catalysts to lower the PCDD/PCDF emission, or as combined catalysts to also simultaneously reduce nitrogen oxides and oxidise halogenated compounds. In the latter case the catalysts volume has to be increased accordingly. Since SCR catalysts are already in use in power stations and municipal waste combustors (MWCs) and have proven their resistance against catalyst poisoning, this technique for the reduction of PCDD/PCDF emissions from MWCs can be easily applied on a full technical scale.

Introduction

At the 6th International Dioxin Symposium at Fukouka we reported upon the catalytic effects of filter ash on the decomposition of PCDD/PCDF /1,2/. Subsequently we investigated the source of this catalytic activity in filter ash. We found that every metal and metal oxide tested exhibited some catalytic activity in the decomposition of PCDD/PCDF in the temperature range of 250 to 350°C. In extensive laboratory tests we evaluated the conditions under which not only PCDD/PCDF could be decomposed by oxidation catalysts in the presence of oxygen, but also organochlorine compounds in general without the formation of PCDD/PCDF /3/. In order to apply these findings to the reduction of PCDD/PCDF emissions from waste incineration facilities effective PCDD/PCDF decomposition in the temperature range of 250 to 350°C appeared to be essential since this catalytic oxidation is best installed as the final gas cleaning device. We found in our laboratory tests that SCR catalysts of the titanium oxide, ferric oxide and zeolithe type in combination with the usual additions of other metal oxides are also very good oxidation catalysts for organochlorine compounds when applied in the absence of ammonia or at low ammonia concentrations. Some of these catalysts exhibit this property very efficiently at the desired temperature range of 250 to 350°C.

We therefore tested such catalysts in pilot plant studies at municipal waste incinerators.

Laboratory experiments

With the model compounds hexachlorobenzene, 2,4,8-trichlorodibenzofuran and tetrachloroethene, the efficiency of decomposition with oxidation catalysts was tested in laboratory experiments. It could be demonstrated that in the temperature range of 200-500°C and space velocities of about 2000 h⁻¹ these compounds can be successfully decomposed in the presence of oxygen (air) and water without the formation of PCDD/PCDF /3/. We could also demonstrate that PCDD/PCDF are much more readily decomposed than hexachlorobenzene or tetrachloroethene.

Tetrachloroethene therefore proved to be a very good model compound in laboratory tests of the temperature dependence of the decomposition efficiency of oxidation catalysts for organochlorine compounds. While most of the commercially available oxidation catalysts tested show only limited efficiency below 350°C, the SCR catalysts on titanium oxide basis with dotations of vanadium oxide exhibit good efficiencies at temperatures as low as 250°C. This is shown in Figure 1. Here three different "low dust" deNOx catalysts are compared with one "high dust" deNOx catalyst. While at high temperature (>400°C) there is little difference in the decomposition efficiency of the four catalysts, distinct differences are apparent at temperatures below 300°C.

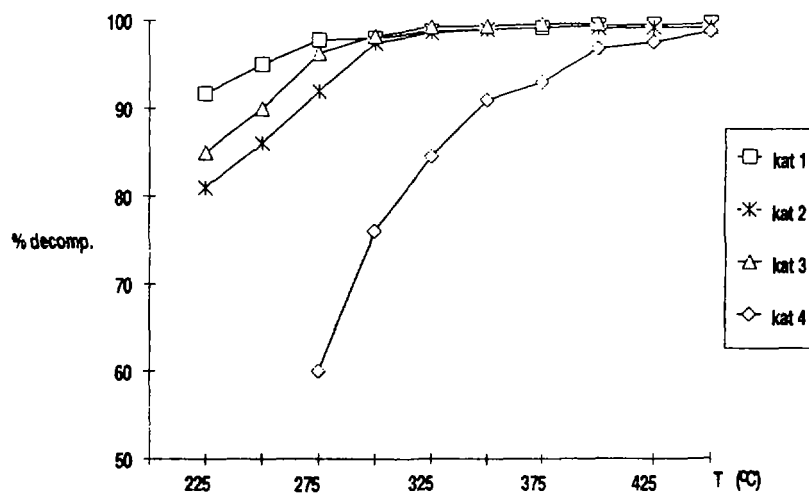


Figure 1: Temperature dependence of hexachloroethene decomposition by catalytic oxidation on deNOx catalysts. Kat 1 to Kat 3 "low dust"-type on TiO₂ basis. Kat 4 "high dust"-type on TiO₂ basis. Air/20% H₂O with 300 ppm hexachloroethene; space velocities 2000 h⁻¹.

It has been shown that there also exists a good correlation between the SO₂ oxidation rates of individual catalysts and their efficiency in PCDD/PCDF decomposition [4]. Therefore the SO₂ to SO₃ conversion factor of the individual catalyst is also a good indicator for its efficiency in PCDD/PCDF decomposition.

Pilot plant studies

The laboratory experiments suggested that oxidation catalysts of the SCR type could be successfully used for the reduction of stack gas emissions of PCDD/PCDF and related compounds in waste incineration plants. Thus at three different waste incinerators pilot facilities, originally installed for the test of SCR catalysts with regard to NOx reduction, were used to test the reduction of PCDD/PCDF and related compounds. A side stream of the off-gas in the range of 100 to 250 m³/h was diverted through the catalytic reactor after preheating to the desired test temperature. The catalyst volume was divided into various parts, so that the influence of the catalyst volume could be evaluated in addition to temperature, catalyst configuration and NH₃-addition to the flue gas. In case of small catalyst volumes (high space velocities) and addition of NH₃ just the denox reaction took place while the decomposition of PCDD/PCDF was suppressed. In the absence of NH₃ or at NH₃ concentrations of a few ppm, under otherwise identical conditions, the PCDD/PCDF reduction was >95% [4].

This means that in order to obtain the necessary reduction in PCDD/PCDF emissions by catalytic oxidation in combination with NOx reduction one has to increase the volume of the catalytic reactor to obtain sufficient catalytic volume for the oxidation reaction.

Examples from	Test I		Test II		Test IIIa		Test IIIb	
	in	out	in	out	in	out	in	out
	ng/Nm ³	ng/Nm ³	ng/Nm ³	ng/Nm ³	ng/Nm ³	ng/Nm ³	ng/Nm ³	ng/Nm ³
∑ Cl ₄ DD	8.5	0.18	23.9	0.19	0.07	0.03	0.023	n.d.
∑ Cl ₅ DD	13.6	0.45	25.2	0.37	1.09	0.05	0.029	n.d.
∑ Cl ₆ DD	21.4	0.64	27.2	0.55	3.66	0.06	0.068	0.032
∑ Cl ₇ DD	63.8	1.56	18.4	0.44	2.68	0.09	0.056	0.038
Cl ₈ DD	136.2	4.03	8.3	0.41	1.20	0.06	0.113	0.031
∑ PCDD	243.5	6.86	103.0	1.96	8.70	0.29	0.289	0.101
∑ Cl ₄ DF	114.5	2.00	28.8	0.36	1.65	0.62	0.353	0.087
∑ Cl ₅ DF	74.4	1.84	20.4	0.53	5.08	0.45	0.384	0.074
∑ Cl ₆ DF	39.7	1.12	9.6	0.35	6.21	0.16	0.503	0.033
∑ Cl ₇ DF	56.2	1.27	5.1	0.24	3.09	0.14	0.258	0.013
Cl ₈ DF	22.1	0.44	0.5	0.10	0.69	n.d.	0.041	n.d.
∑ PCDF	306.9	6.67	64.4	1.58	16.72	1.37	1.539	0.207
2,3,7,8-Cl ₄ DD	0.53	0.009	0.17	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3,7,8-Cl ₅ DD	1.41	0.04	0.47	0.005	0.039	n.d.	n.d.	n.d.
1,2,3,4,7,8-Cl ₆ DD	1.43	0.03	0.58	0.011	0.039	n.d.	0.007	0.004
1,2,3,6,7,8-Cl ₆ DD	1.82	0.04	1.24	0.036	0.184	0.002	0.008	0.006
1,2,3,7,8,9-Cl ₇ DD	1.30	0.03	0.68	0.025	0.123	0.002	0.006	n.d.
1,2,3,4,6,7,8-Cl ₇ DD	31.98	0.82	9.67	0.250	0.878	0.048	0.029	0.051
2,3,7,8-Cl ₄ DF	3.73	0.07	0.63	0.018	0.106	0.013	0.012	0.006
1,2,3,7,8-Cl ₅ DF	4.77	0.15	1.53	0.035	0.167	0.033	0.052	0.007
2,3,4,7,8-Cl ₆ DF	4.28	0.10	1.17	0.023	0.233	0.024	0.038	0.005
1,2,3,4,7,8-Cl ₆ DF	4.46	0.13	0.97	0.037	0.495	0.014	0.073	0.005
1,2,3,6,7,8-Cl ₆ DF	4.51	0.13	1.09	0.041	0.800	0.030	0.089	0.005
1,2,3,7,8,9-Cl ₇ DF	0.26	n.d.	0.06	0.004	0.038	0.003	n.d.	n.d.
2,3,4,6,7,8-Cl ₇ DF	3.15	0.10	0.73	0.030	0.953	0.013	0.053	0.003
1,2,3,4,6,7,8-Cl ₇ DF	41.45	0.93	3.96	0.210	1.820	0.090	0.204	0.013
1,2,3,4,7,8,9-Cl ₇ DF	2.67	0.08	0.13	0.006	0.370	0.008	0.016	n.d.
TEQ (BCA)	7.01	0.17	2.498	0.053	0.499	0.027	0.047	0.007
TEQ (NATO/CCMS)	6.60	0.16	1.811	0.041	0.451	0.023	0.049	0.006
% reduction in TEQ (NATO/CCMS)	97.5		97.7		94.9		86.9	

Table 1: PCDD/PCDF-analyses of waste incinerator off-gases before (in) and after (out) catalytic oxidation. Examples from test series with a range of initial concentrations.

Representative results for different starting concentrations of PCDD/PCDF are shown in detail in Table 1. The test IIIb shows that even under very low starting concentrations a reduction of PCDD/PCDF concentration was obtained. This demonstrates that under the conditions of catalytic oxidation in the temperature range of 250 to 350°C no relevant PCDD/PCDF de novo synthesis had occurred.

In Figure 2 residual PCDD/PCDF concentrations after catalytic oxidation from a range of initial concentrations in relation to the catalyst volume are shown. In the concentration range of interest the relative reduction in PCDD/PCDF concentration under comparable conditions was slightly dependent on the initial concentration. This means that in order to obtain a final concentration of <0.1 ng TEQ/m³, the surface of the catalytic reactor has to be adjusted according to the expected initial concentration range. Further optimization appears possible by adjusting the catalyst configuration and/or the reaction temperature.

Under comparable conditions no substantial difference in the degree of PCDD/PCDF reduction could be detected between new catalysts and those which had been used for 6000 h under both denox conditions and oxidation

adsorptive effects. Analyses of catalyst material after use for more than 6000 h in the pilot facility did also not show any accumulation of PCDD/PCDF by adsorption.

PCBs, chlorobenzenes and chlorophenols were shown to be reduced by catalytic oxidation to the same extent as reported here for PCDD/PCDF.

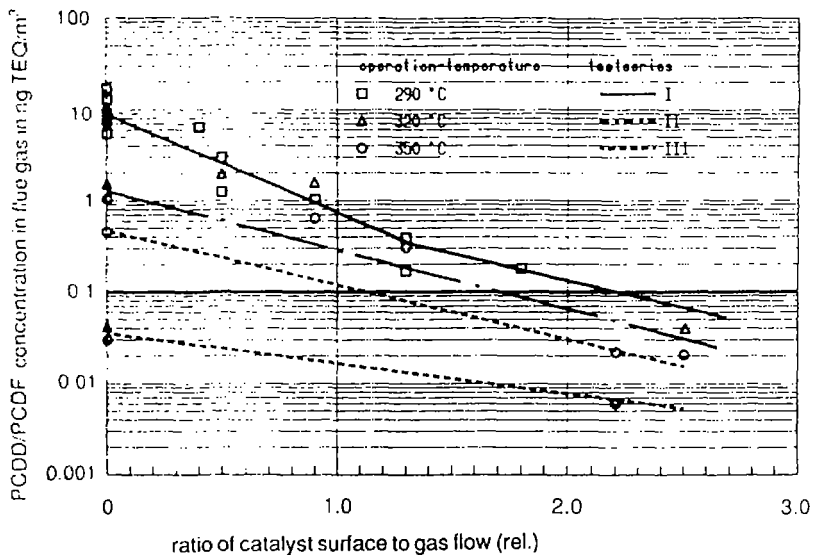


Figure 2: Residual concentrations after catalytic oxidation in relation to the outer catalyst surface. The inlet concentrations of PCDD/PCDF are the values at catalyst volume zero, the outlet concentrations are correlated to different catalyst sizes.

Conclusions

Laboratory tests and pilot studies at waste incinerators have shown that catalysts of the SCR type, especially those on TiO₂ basis, are also excellent oxidation catalysts for the decomposition of PCDD/PCDF and related compounds. PCDD/PCDF levels <0.1 ng TEQ/m³ in stack gas were obtained in pilot plant studies using SCR catalysts.

Simultaneous reduction of NO_x and PCDD/PCDF requires additional catalyst volume either before or after the denox reaction.

No de novo synthesis of PCDD/PCDF and no accumulation of PCDD/PCDF in the catalytic reactor was observed under the conditions employed

References

- 1) H. Hagenmaier, M. Kraft, H. Brunner, R. Haag, 6th International Symposium on Chlorinated Dioxins and Related Compounds, Fukuoka 1986
- 2) H. Hagenmaier, M. Kraft, H. Brunner, R. Haag, *Environ. Sci. Technol.* **21**, 1080-1084 (1987)
- 3) H. Hagenmaier, VDI-Berichte 730, 239-254 (1989)
- 4) H. Hagenmaier, G. Mittelbach, *VGB Kraftwerkstechnik*, **70**, 491-493 (1990)