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# Perovskite-type oxide monolithic catalysts for combustion of chlorinated hydrocarbons

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**Abstract**

The catalytic activity of perovskite-coated and perovskite-extruded monolithic catalysts was studied in the total oxidation of several aliphatic chlorinated hydrocarbons. At low reaction temperatures a reversible catalyst deactivation takes place. The complete decomposition of the chlorinated hydrocarbons without formation of by-products depends on the reaction conditions, the kind of chlorinated hydrocarbon and the monolith preparation. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The destruction of volatile organic compounds by catalytic combustion has been widely utilized in several technical processes. The function of the catalyst is to convert the polluting compounds into relatively harmless compounds at low operating temperatures and high space velocities. In the case of chlorinated hydrocarbons the desired reaction is the total oxidation to $H_2O$, $CO_2$ and HCl without formation of by-products [1,2]. Supported precious metal and mixed oxide catalysts in pelleted form or fixed on monoliths are applied usually for the purification of chlorinated compounds contaminated waste gas streams [1–5].

Perovskite-type oxides ($ABO_3$) containing Ln (Ln=rare-earth metals) partially substituted by Sr in A position and Mn, Fe, Co in B position have been found to be effective catalysts for the total oxidation of hydrocarbons and oxygenated compounds [6,7]. In previous papers it was found that bulk perovskites (A=La, Sr; B=Mn,Co) decompose chloromethane, dichloromethane and 1,2 dichloroethane completely in air without deactivation at temperatures above 550°C [8,9]. In the present work the properties of perovskite monolithic catalysts in the combustion of different chlorinated hydrocarbons were studied. Perovskite-coated and perovskite-extruded monolithic catalysts were compared.

## 2. Experimental

### 2.1. Catalyst preparation

For all investigations a perovskite of the composition $La_{0.84}Sr_{0.16}Mn_{0.67}Co_{0.33}O_{3+\delta}$ was applied.

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Perovskite-coated monolithic catalysts were obtained in a two-step procedure: Impregnation of a monolithic cordierite ceramic support (cell density: 200 csi, diameter: 20 mm, length: 50 mm) with a solution containing appropriate amounts of the corresponding nitrates. After calcination at 600°C in air the impregnated monoliths were coated with a bulk perovskite–Tylose®–water suspension. The dried samples were calcined at 600°C in air. After calcination the monolith support contained 9.8 wt% perovskite. The used bulk perovskites were obtained by precipitation [8].

Perovskite-extruded monolithic catalysts were obtained by extrusion of a mixture of precipitated perovskites (calcined at 600°C) and cordierite precursor material in monolithic form (cell density: 200 csi, diameter: 20 mm, length: 50 mm). The calcination of the dried samples was carried out at 550°C in air. After calcination the monolith contained 25 wt% perovskite, the specific surface area amounted to 57 $m^2/g$.

### 2.2. Catalytic measurements

The catalytic measurements were carried out in a fixed bed microreactor. The combustion of $CH_4$, $CH_3Cl$, $CH_2Cl_2$ and $CH_2Cl$–$CH_2Cl$ (0.1–1.0 vol% in air) was investigated. The GHSV (gas hour space velocity) was calculated with respect to the total volume of the monolith.

The exit gas composition was quantitatively analyzed by on line GC (FID, TCD) and of line-GC–MS-analytical systems.

## 3. Results and discussion

In previous studies on bulk perovskite-type oxides we have shown that in contrast to hydrocarbons the total oxidation of chlorinated hydrocarbons (CHC) involves a reversible deactivation of the catalysts [8–10]. Depending on the reaction temperature, GHSV and the kind of CHC a nearly constant conversion level is reached after an initial period of about 45 min. In additional experiments it could be shown that the catalyst can be regenerated in a stream of nitrogen or air at temperatures above 300°C. At higher temperatures (e.g. $CH_3Cl$: above 550°C) complete conversion was observed without catalyst deactivation within a period of time up to 250 h [9].

In Fig. 1 the conversion levels of several CHC and of methane at steady state conditions are shown using a perovskite-coated monolith as a function of the reaction temperature for two different concentrations of CHC. The reactivity of the CHC decreases in the order $CH_2Cl$–$CH_2Cl$>$CH_2Cl_2$>$CH_3Cl$≈$CH_4$. The complete conversion of $CH_2Cl$–$CH_2Cl$ takes place at markedly lower temperatures. Similar results were obtained using supported precious metal catalysts [2]. The concentration of the CHC in the feed does not influence significantly the conversion levels at higher reaction temperatures. In the low-temperature range higher conversion levels were observed for the series with 0.1 vol% CHC as compared to that with 1.0 vol% CHC.

The main reaction products are $CO_2$, HCl and $H_2O$. CO and $COCl_2$ were not detected. At lower reaction temperatures (lower conversion levels) besides unreacted CHC several higher chlorinated hydrocarbons and chlorine were found as by-products in the exit gas. Their amount depends on the reaction conditions and the kind of CHC. Polychlorinated dibenzodioxines and furanes could not be identified [8,9].

In Table 1 the concentration of chlorinated by-products in the exit gas is presented as a function of the reaction temperature and the kind of CHC in the feed. In general, higher chlorinated hydrocarbons, cleavage and condensation products are formed. With a $CH_2Cl$–$CH_2Cl$ feed no decomposition products were detected in the exit gas at reaction temperatures above 550°C. At lower reaction temperatures chloromethanes, chloroethylenes and condensation products (chloropropylenes) are formed. Smaller amounts of by-products in the lower reaction temperature range were found with $CH_3Cl$ and $CH_2Cl_2$ in the feed. However, these by-products are not destructed completely at temperatures up to 600°C. The quantities of the formed by-products are significantly lower with 0.1 vol% CHC in the feed.

Fig. 2 shows the effect of the reaction temperature on the conversion of several CHC and methane at steady state conditions on a perovskite-extruded monolithic catalyst. In comparison to the perovskite-coated monolithic catalyst the same conversion levels are reached at markedly lower reaction

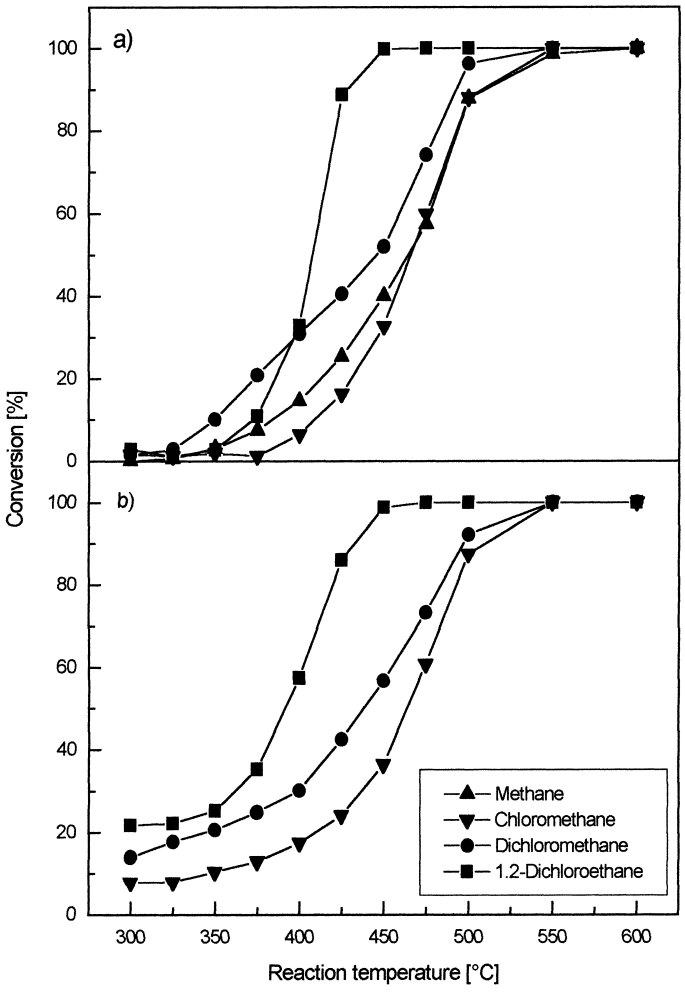


Fig. 1. Conversion of chlorinated hydrocarbons and methane on perovskite-coated monolithic catalyst: (a) 1 vol%, and (b) 0.1 vol% in 5 l/h air (GHSV=320 $h^{-1}$).

temperatures. The higher catalytic activity of the perovskite-extruded monolithic catalyst as compared to the perovskite-coated catalyst is caused by the higher content of active perovskite and their higher specific surface area within the perovskite-extruded monolith. The order of reactivity of the CHC is comparable to that obtained with perovskite-coated monoliths. Remarkably lower concentrations of by-products in the exit gas were found (Table 2). Above a reaction temperature of 475°C only traces of by-products were detected. The kind of the by-products are qualitatively the same as observed on perovskite-coated monoliths. Furthermore, small amounts of chlorine were detected. CO and $COCl_2$ could not be identified. There are no indications for the formation of polychlorinated dibenzodioxines and dibenzofuranes.

The influence of the space velocity on the conversion of $CH_2Cl_2$ on the perovskite-extruded monolithic catalyst is represented in Fig. 3. The results show that the conversion of $CH_2Cl_2$ increased with decreasing space velocity. In Table 3 the corresponding concentrations of the by-products are given. It can be clearly seen that the number of by-products decreases with increasing space velocity, whereas their concentrations increase.

Table 1
Concentration of chlorinated by-products in exit gas (vpm) on perovskite-coated monolithic catalyst as a function of the reaction temperature (according to Fig. 1)

| | Reaction temperature (°C) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 300 | 350 | 400 | 425 | 450 | 475 | 500 | 550 | 600 |
| 1.0 vol% | | | | | | | | | |
| *Chloromethane* | | | | | | | | | |
| Dichloromethane | 10 | 56 | 255 | 511 | 1015 | 1641 | 1500 | 13 | 0 |
| Trichloromethane | 0 | 0 | 0 | 25 | 91 | 342 | 890 | 0 | 0 |
| Tetrachloromethane | 0 | 0 | 0 | 0 | 0 | 27 | 163 | 456 | 45 |
| Trichloroethylene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 44 | 13 |
| Tetrachloroethylene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 104 | 237 |
| *Dichloromethane* | | | | | | | | | |
| Trichloromethane | 37 | 150 | 359 | 667 | 1275 | 2004 | 1606 | 0 | 0 |
| Tetrachloromethane | 0 | 0 | 0 | 31 | 103 | 350 | 1154 | 524 | 79 |
| Trichloroethylene | 0 | 0 | 0 | 0 | 0 | 13 | 18 | 48 | 13 |
| Tetrachloroethylene | 0 | 0 | 0 | 0 | 0 | 0 | 18 | 145 | 416 |
| *1,2-Dichloroethane* | | | | | | | | | |
| Chloromethane | 86 | 293 | 1877 | 3259 | 1122 | 139 | 8 | 0 | 0 |
| Trichloromethane | 0 | 0 | 12 | 59 | 126 | 23 | 0 | 0 | 0 |
| Tetrachloromethane | 0 | 0 | 17 | 45 | 119 | 390 | 440 | 40 | 0 |
| *trans*-1,2-Dichloroethylene | 0 | 0 | 354 | 2070 | 2311 | 779 | 120 | 0 | 0 |
| Trichloroethylene | 0 | 0 | 0 | 79 | 408 | 519 | 306 | 26 | 0 |
| Tetrachloroethylene | 0 | 28 | 231 | 404 | 87 | 0 | 0 | 0 | 0 |
| 1-Chloro-1-propylene | 0 | 0 | 0 | 15 | 78 | 39 | 0 | 0 | 0 |
| 3-Chloro-1-propylene | 0 | 37 | 616 | 2610 | 2744 | 972 | 149 | 0 | 0 |
| 0.1 vol% | | | | | | | | | |
| *Chloromethane* | | | | | | | | | |
| Dichloromethane | 0 | 0 | 23 | 41 | 106 | 110 | 108 | 0 | 0 |
| Trichloromethane | 0 | 0 | 0 | 0 | 0 | 16 | 44 | 0 | 0 |
| Tetrachloromethane | 0 | 0 | 0 | 0 | 0 | 0 | 6 | 31 | 0 |
| Tetrachloroethylene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 |
| *Dichloromethane* | | | | | | | | | |
| Trichloromethane | 0 | 18 | 55 | 73 | 93 | 123 | 120 | 0 | 0 |
| Tetrachloromethane | 0 | 0 | 0 | 0 | 0 | 18 | 40 | 15 | 0 |
| Trichloroethylene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 16 | 18 |
| Tetrachloroethylene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 23 |
| *1,2-Dichloroethane* | | | | | | | | | |
| Chloromethane | 26 | 44 | 140 | 174 | 110 | 57 | 310 | 0 | 0 |
| Tetrachloromethane | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 | 0 |
| *trans*-1,2-Dichloroethylene | 0 | 0 | 20 | 41 | 42 | 29 | 16 | 0 | 0 |
| Tetrachloroethylene | 0 | 0 | 15 | 19 | 0 | 0 | 0 | 0 | 0 |
| 3-Chloro-1-propylene | 0 | 0 | 35 | 55 | 51 | 35 | 19 | 0 | 0 |

## 4. Conclusions

The deactivation of the perovskite monolithic catalysts is attributed to a reversible blocking of active sites on the catalysts by educts, intermediates or reaction products. The formation of metal chlorides and -oxychlorides on the surface and in the bulk phase could be detected by X-ray powder diffractometry and

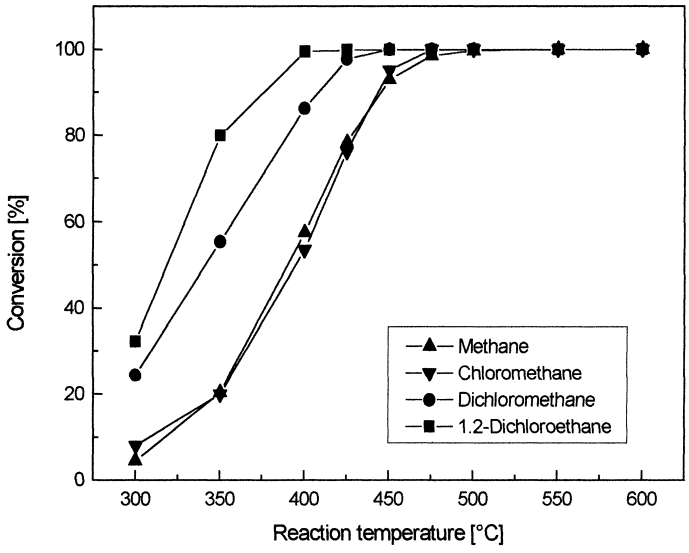


Fig. 2. Conversion of chlorinated hydrocarbons and methane on perovskite-extruded monolithic catalyst (GHSV=320 $h^{-1}$; 1 vol% in 5 l/h air).

Table 2
Concentration of chlorinated by-products in exit gas (vpm) on perovskite-extruded monolithic catalyst as a function of the reaction temperature (according to Fig. 2)

| | Reaction temperature (°C) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 300 | 350 | 400 | 425 | 450 | 475 | 500 | 550 | 600 |
| *Chloromethane* | | | | | | | | | |
| Dichloromethane | 0 | 29 | 255 | 512 | 432 | 18 | 0 | 0 | 0 |
| Trichloromethane | 0 | 0 | 0 | 12 | 47 | 41 | 0 | 0 | 0 |
| Tetrachloromethane | 0 | 0 | 0 | 0 | 0 | 16 | 0 | 0 | 0 |
| *Dichloromethane* | | | | | | | | | |
| Chloromethane | 404 | 382 | 5 | 0 | 0 | 0 | 0 | 0 | 0 |
| Trichloromethane | 6 | 16 | 68 | 158 | 0 | 0 | 0 | 0 | 0 |
| Tetrachloroethylene | 0 | 0 | 3 | 20 | 3 | 2 | 0 | 0 | 0 |
| α-Chlorotoluene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 65 | 52 |
| *1,2-Dichloroethane* | | | | | | | | | |
| Chloromethane | 820 | 2889 | 836 | 3 | 1 | 2 | 1 | 2 | 0 |
| Dichloromethane | 0 | 3 | 6 | 0 | 0 | 0 | 0 | 0 | 0 |
| Trichloromethane | 0 | 4 | 3 | 3 | 0 | 0 | 0 | 0 | 0 |
| Tetrachloromethane | 2 | 0 | 0 | 43 | 0 | 0 | 0 | 0 | 0 |
| Trichloroethylene | 0 | 4 | 198 | 686 | 11 | 1 | 0 | 0 | 0 |
| Tetrachloroethylene | 2 | 0 | 55 | 1602 | 332 | 33 | 4 | 3 | 0 |

EPMA measurements [8]. The dependence on the reaction temperature indicates an equilibrium between the concentration of metal chlorides on the surface and the partial pressure of water in the gas phase.

$$2Cl^- + H_2O \rightleftarrows -O^{2-} + 2HCl$$

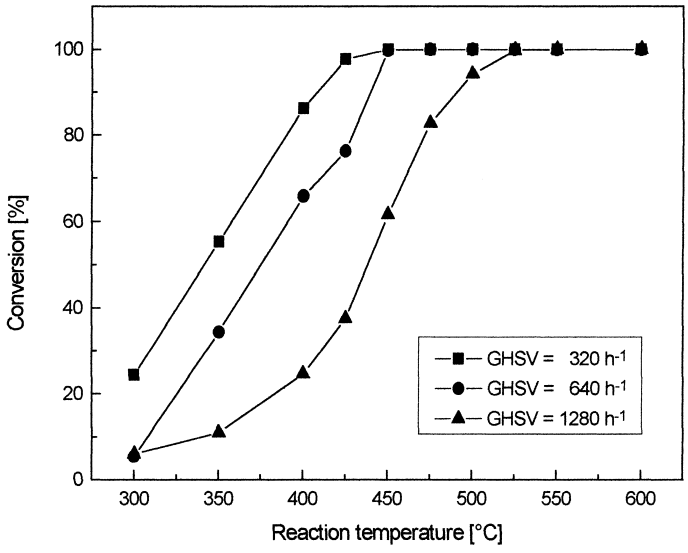


Fig. 3. Conversion of dichloromethane on perovskite-extruded monolithic catalyst at different GHSV (1 vol% dichloromethane in air).

Table 3
Influence of the GHSV on the concentration of chlorinated by-products in exit gas (vpm) in the oxidation of $CH_2Cl_2$ on perovskite-extruded monolithic catalyst

| | Reaction temperature (°C) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 300 | 350 | 400 | 425 | 450 | 475 | 500 | 550 | 600 |
| *GHSV=320 $h^{-1}$; total feed 5000 ml/h* | | | | | | | | | |
| Chloromethane | 404 | 382 | 5 | 0 | 0 | 0 | 0 | 0 | 0 |
| Trichloromethane | 6 | 16 | 68 | 158 | 0 | 0 | 0 | 0 | 0 |
| Tetrachloromethane | 0 | 0 | 3 | 20 | 3 | 2 | 0 | 0 | 0 |
| α-Chlorotoluene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 65 | 52 |
| *GHSV=640 $h^{-1}$; total feed 10 000 ml/h* | | | | | | | | | |
| Chloromethane | 174 | 314 | 99 | 12 | 0 | 0 | 0 | 0 | 0 |
| Trichloromethane | 0 | 14 | 44 | 229 | 51 | 0 | 0 | 0 | 0 |
| Tetrachloroethylene | 0 | 0 | 0 | 0 | 25 | 0 | 0 | 0 | 0 |
| *GHSV=1280 $h^{-1}$; total feed 20 000 ml/h* | | | | | | | | | |
| Chloromethane | 60 | 117 | 93 | 37 | 22 | 35 | 31 | 33 | 24 |
| Trichloromethane | 0 | 0 | 46 | 142 | 238 | 204 | 123 | 0 | 0 |

$$-OH^- + -Cl^- \rightleftarrows -O^{2-} + HCl$$

At increasing reaction temperature the fraction of the metal chloride phases on the surface and in the bulk drops.

The results obtained by the analysis of the exit gas composition can be explained by successive insertion of chlorine species in intermediate compounds on the catalyst surface. The insertion reaction should be controlled by the kinetic factors, because the number and the content of higher chlorinated hydrocarbons in the exit gas depends on the time on stream and reaction temperature. Besides chlorine insertion, cleavage and condensation reactions take place in the

presence of perovskite catalysts. At higher reaction temperatures the chlorinated by-products cannot be formed under the reaction conditions.

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