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# Supported perovskite-type oxide catalysts for the total oxidation of chlorinated hydrocarbons

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**Abstract**

The catalytic behaviour of supported (zirconia, cordierite monoliths) and unsupported $AMnO_3$ (A = La, Didym-Di) perovskites was studied in the total oxidation of chlorinated hydrocarbons (CHC). By-products (higher chlorinated hydrocarbons, lower molecular coupling and cracking products) were formed at reaction temperatures $<550^\circ C$. Porous zirconia as support enhances the catalytic activity at low perovskite contents and diminishes the by-product formation. The preparation method (impregnation or precipitation-deposition of perovskites on zirconia and impregnation and coating of cordierite monoliths with perovskites) influences catalytic activity and by-product formation. $LaMnO_3$ and $DiMnO_3$ perovskite-type oxides reveal similar catalytic behaviour. ©1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Perovskite-type oxides; Zirconia; Cordierite monoliths; Total oxidation; Chlorinated hydrocarbons

## 1. Introduction

The destruction of volatile organic compounds into environmentally harmless substances by catalytic combustion is used in several industrial processes. Supported precious metal and mixed oxide catalysts in pelleted form or supported on refractory oxides as well ceramic monoliths are applied usually for the total oxidation of chlorinated hydrocarbons (CHC) in waste gas streams [1,2].

Perovskite-type oxides with the general formula $ABO_3$ (A represents a lanthanoide and/or alkaline-earth metal ion and B a transition metal ion) have been found to be effective catalysts for the total oxidation of hydrocarbons and oxygenated compounds [3–5]. The most catalytically active perovskites contain La partially substituted by Sr in the A-position and Co and/or Mn in the B-position mainly. In order to obtain catalysts with a high dispersity supported perovskites have been investigated.

Perovskites supported on zirconia, alumina, $La_2O_3{\cdot}19Al_2O_3$ or ceria were tested for the complete oxidation of methane and propane [6,7] and for the Denox-process [8]. Fujii et al. [7] found a significant increase of the catalytic activity of $La_{0.8}Sr_{0.2}CoO_3$ supported on zirconia. Perovskites supported on cordierite monoliths were investigated in the total oxidation of methane, propane and carbon monoxide [9–11].

In previous studies it was shown that $ABO_3$ perovskites (A = La, Sr; B = Mn, Co) are effective catalysts for total oxidation of CHC [12,13]. The destruction of CHC is associated with deactivation of the catalyst due to blocking of catalytically active sites by reactants and/or structural changes [1,2,14–18].

The aim of the present work was to investigate the influence of the support material (zirconia or cordierite monoliths) on the properties of $AMnO_3$

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perovskite-type oxides (A = La, Didym–Di) in the total oxidation of CHC considering catalyst deactivation and formation of by-products. Furthermore, the catalytic activity of $AMnO_3$ perovskites with La and Di in A-position was compared. Didym oxide (67.7 wt.% $Nd_2O_3$, 21.6 wt.% $Pr_6O_{11}$ and 10.7 wt.% $La_2O_3$) as cheap rare-earth component is of interest from the technical point of view for the preparation of the catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

The perovskite-type oxides were prepared from the corresponding nitrates by coprecipitation of the hydroxides with 1 N sodium hydroxide solution and hydrogen peroxide at pH 9.1 and 50°C (molar ratio of B(II) ions to hydrogen peroxide = 1.8). The precipitates were aged for 0.25 h, filtered off, washed, dried and calcined in air at 600°C for 6 h.

The support material zirconia ($S_{BET} = 78\,m^2\,g^{-1}$) was prepared by precipitation from an aqueous solution of $ZrO(NO)_3$ and ammonia at pH 8.4 and room temperature. The dried precipitate was calcined in air at 500°C for 6 h. Perovskite zirconia catalysts were obtained by precipitation-deposition (coprecipitation of the appropriate hydroxides on zirconia) or by wet impregnation of the perovskite component on the support with an aqueous solution containing the appropriate amounts of the corresponding nitrates. The catalyst precursors were calcined in air at 600°C for 6 h. The perovskite content on zirconia amounted to 5, 10 or 20 mol%.

Perovskite catalysts supported on ceramic cordierite monoliths (length = 5 cm, diameter = 1.9 cm, 200 csi) were prepared by impregnation with a solution of the adequate nitrates followed by coating with a perovskite-tylose®-water suspension. The impregnated and dried monoliths were calcined in air at 600°C for 6 h.

### 2.2. Catalyst characterization

The phase analysis of the perovskite and perovskite zirconia catalysts was carried out by powder X-ray diffractometry (XRD). The specific surface areas of the calcined catalysts were determined by $N_2$-adsorption (BET-method) before and after reaction with CHC.

### 2.3. Catalytic measurements

The catalysts were tested in the total oxidation of 0.1 and 1.0 vol% chloromethane and dichloromethane, resp. in air ($5\,l\,h^{-1}$) in a fixed bed microreactor at reaction temperatures between 300 and 650°C (GHSV = $2300\,h^{-1}$ (monolithic catalysts) and W/F = $0.432\,g\,s\,ml^{-1}$ (bulk catalysts)). GHSV was calculated with respect to the catalysts volume. The amount of bulk catalysts loaded was 0.6 g (particle size diameter: 0.1–0.315 mm). The exit gas composition was quantitatively analyzed by on-line GC (FID/TCD) and off-line GC-MS analytical systems.

## 3. Results and discussion

The complete oxidation of CHC on metal oxides is connected with a catalyst deactivation as shown in several papers [1,2,14–18]. Reversible and irreversible deactivation phenomena were observed on perovskite-type oxide catalysts. In contrast to the $LaMnO_3$ perovskites a complete destruction of the perovskite structure during the conversion of CHC was found on $LaCoO_3$ perovskites. The formation of LaOCl and $Co_3O_4$ via volatile $CoCl_2$ was stated [12]. In the case of $LaMnO_3$ perovskites after an initial period of up to 60 min a nearly constant reaction rate is reached. Within an investigated reaction time of 250 h no catalyst deactivation was observed.The following presented results are those at steady state conditions. The total oxidation of chloromethane as test reaction was investigated mainly because of the high stability of chloromethane compared with other CHC [14].

In Fig. 1 the conversion degrees of chloromethane on $LaMnO_3$ and $DiMnO_3$ perovskites are shown as a function of the reaction temperature for two feed concentrations. It can be seen that the catalytic activity of the didym containing sample is higher at a feed concentration of 1 vol%. No significant differences between $LaMnO_3$ and $DiMnO_3$ perovskites were observed for a feed concentration of 0.1 vol% chloromethane.

Table 1
Specific surface areas ( $m^2 g^{-1}$) of $AMnO_3$ and $AMnO_3$-$ZrO_2$ catalysts prepared by impregnation and precipitation-deposition

| | | Calcination temperature | | | |
|---|---|---|---|---|---|
| | | 600°C | | 800°C | |
| | *x* (mol% perovskite) | Impregnation | Precipitation-deposition | Impregnation | Precipitation-deposition |
| $LaMnO_3$-$ZrO_2$ | 0 | 78 | | | |
| | 5 | 57 (47)[a] | 52 | 50 (38)[a] | 30 |
| | 10 | 50 | 42 | 43 | 29 |
| | 20 | 38 | 47 | 32 | 29 |
| $DiMnO_3$-$ZrO_2$ | 5 | 55 (45) | – | 42 (38)[a] | |
| | | Precipitation | | | |
| $LaMnO_3$ | | 37 (16)[a] | 18 (14)[a] | | |
| $DiMnO_3$ | | 46 (17)[a] | 19 (13)[a] | | |

[a] After reaction with 1 vol% chloromethane in air at 650°C.

Table 2
Concentration of chlorinated by-products in exit gas (vpm) in the oxidation of chloromethane (according to Fig. 1)[a]

| Catalyst | Reaction temperature/°C | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 325 | 350 | 375 | 400 | 425 | 450 | 475 | 500 | 550 |
| *LaMnO₃* | | | | | | | | | |
| $CH_2Cl_2$ | 125 | 220 | 360 | 590 | 840 | 1050 | 1250 | 1400 | 410 |
| $CHCl_3$ | – | – | 10 | 25 | 55 | 100 | 160 | 250 | 510 |
| $CCl_4$ | – | – | – | – | – | 10 | 20 | 30 | 130 |
| *DiMnO₃* | | | | | | | | | |
| $CH_2Cl_2$ | 320 | 560 | 860 | 1170 | 1450 | 1680 | 1670 | 1380 | – |
| $CHCl_3$ | – | 15 | 85 | 220 | 260 | 270 | 260 | 120 | – |
| $CCl_4$ | – | – | – | 10 | 40 | 80 | 110 | 10 | |

[a] Feed: 1.0 vol% chloromethane in air, W/F = 0.43 gs $ml^{-1}$.

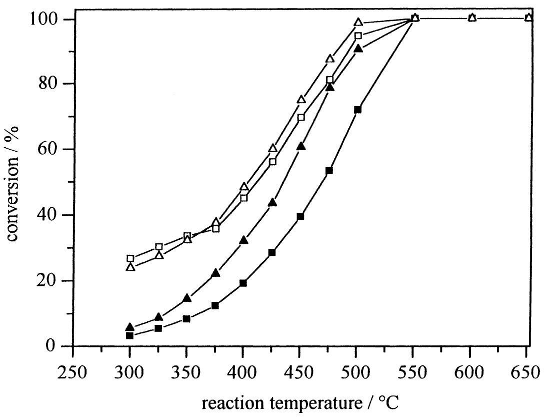

Fig. 1. Conversion of chloromethane on $AMnO_3$ ($LaMnO_3$: □,■; $DiMnO_3$: △,▲) catalysts vs. reaction temperature for different feed concentrations ; 600°C; 0.1 (open symbols) and 1 vol% (full symbols) chloromethane in air; W/F: 43.2 gs $ml^{-1}$.

XRD measurements on the investigated samples calcined at 600°C show the diffraction pattern of a poor crystallized $LaMnO_3$ perovskite with small admixtures of $La_2O_2CO_3$. After interaction with chloromethane no significant destruction of the perovskite structure took place. Only small amounts of LaOCl were detected. The appropriate manganese compounds were probably X-ray amorphous and could not be identified. The specific surface areas of the samples decrease significantly after interaction of the perovskites with the reaction products (hydrochloric acid, water, carbon dioxide) because of the partial formation of rare-earth metal and manganese chloride compounds (Table 1).

Table 2 gives a general view about the formed by-products in the total oxidation of 1.0 vol% chloromethane in air on $LaMnO_3$ and $DiMnO_3$. Under the chosen reaction conditions higher chlorinated methanes were formed. The maximum of the by-product formation lies in the temperature range between 400 and 500°C. At higher reaction temperatures (>500°C) the amount of by-products decreases significantly. In this temperature range the by-product formation on $DiMnO_3$ is lower than on $LaMnO_3$ perovskites. Chlorine was formed in small amounts (~700 vpm at 650°C). Neither carbon monoxide, phosgene nor condensed reaction products were found under these reaction conditions. The amount of by-products decreases with the decreasing CHC concentration in the feed.

Perovskite-type oxides supported on zirconia were prepared using impregnation or precipitation-deposition method. In the case of the impregnated $LaMnO_3$-$ZrO_2$ catalysts the specific surface areas decrease with increasing perovskite content (Table 1). For the samples with 5 mol% $LaMnO_3$ or $DiMnO_3$ on zirconia the specific surface areas are shown after interaction with 1 vol% chloromethane in air at 650°C for 2 h. Compared with the unsupported samples the decrease of the specific surface areas is lower.

In Fig. 2 the influence of the preparation method of $LaMnO_3$-$ZrO_2$ catalysts upon the conversion of 1 vol% chloromethane in air is shown. At low perovskite contents a high catalytic activity was found. A decrease of the catalytic activity was observed with increasing perovskite content. The higher catalytic activity of the supported perovskite catalysts is connected with their higher specific surface areas in comparison to the unsupported catalysts (Table 1). The catalytically active perovskite phase is dispersed on the zirconia surface.

In general, the catalysts prepared by precipitation-deposition are more catalytically active than the impregnated ones. Because the textural data of the both investigated catalyst series do not differentiate significantly (Table 1) it is supposed that the structural properties of the supported perovskites play an important role for the catalytic activity. The perovskite phase could be identified by XRD measurements on samples calcined at 600°C and a perovskite content of 20 mol%. For the identification of the perovskite phase a calcination temperature of 1200°C is necessary in the case of the impregnated sample with 5 mol% $LaMnO_3$ on zirconia whereas a calcination temperature of 800°C is sufficient for the precipitated sample [19]. Furthermore, it could be shown by oxygen desorption measurements [19] that the curve profiles of the $LaMnO_3$-$ZrO_2$ catalysts prepared by precipitation-deposition are quite similar to that of the unsupported sample. In the case of the impregnated samples a broad curve profile was observed. From the XRD and oxygen desorption measurements it was concluded that the crystallinity of the supported perovskite component on catalysts prepared by precipitation-deposition is higher than that of the impregnated catalysts. Thus, the results obtained are a reference for the influence of the crystallinity of the perovskite component on the catalytic activity of $LaMnO_3$-$ZrO_2$ in total oxidation of CHC. A higher crystallinity of the perovskite component causes a higher catalytic activity of the supported perovskite-zirconia catalysts.

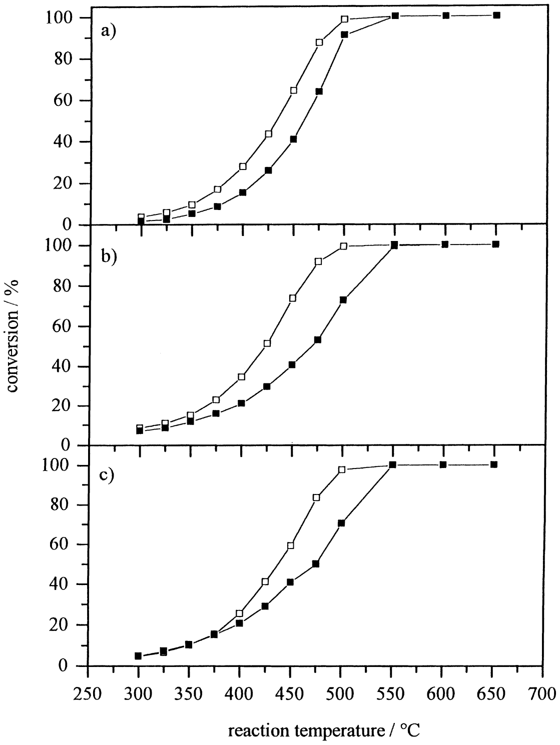

Fig. 2. Influence of the preparation method upon the conversion of chloromethane on $LaMnO_3$-$ZrO_2$ catalysts in dependence on the reaction temperature and the perovskite content x: (a) $x=5$ mol%, (b) $x=10$ mol%, (c) $x=20$ mol% (catalysts prepared by impregnation (■) and precipitation-deposition (□)); 1 vol% chloromethane in air; $W/F=43.2$ gs ml$^{-1}$.

In Table 3 the by-product concentrations in the exit gas of the chloromethane conversion are

Table 3
Concentration of chlorinated by-products in exit gas (vpm) in the oxidation of chloromethane (according to Fig. 2)[a]

| Catalyst (precipitation-deposition method) | Reaction temperature/°C | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 325 | 350 | 375 | 400 | 425 | 450 | 475 | 500 | 550 |
| *5 mol% $LaMnO_3$-$ZrO_2$* | | | | | | | | | |
| $CH_2Cl_2$ | – | – | – | 40 | 110 | 230 | 360 | 170 | – |
| $CHCl_3$ | – | – | – | – | – | – | 30 | 80 | – |
| $CCl_4$ | – | – | – | – | – | – | – | – | – |
| *10 mol% $LaMnO_3$-$ZrO_2$* | | | | | | | | | |
| $CH_2Cl_2$ | – | <10 | 30 | 90 | 210 | 360 | 400 | 150 | – |
| $CHCl_3$ | – | – | – | – | – | 10 | 60 | 80 | – |
| $CCl_4$ | – | – | – | – | – | – | – | <10 | – |
| *20 mol% $LaMnO_3$-$ZrO_2$* | | | | | | | | | |
| $CH_2Cl_2$ | <10 | 10 | 40 | 120 | 290 | 580 | 770 | 300 | – |
| $CHCl_3$ | – | – | – | – | – | 10 | 90 | 240 | 10 |
| $CCl_4$ | – | – | – | – | – | – | – | 30 | – |

[a] Feed: 1.0 vol% chloromethane in air, W/F = 0.43 gs $ml^{-1}$.

summarized for the $LaMnO_3$-$ZrO_2$ catalysts prepared by precipitation-deposition as an example. It can be stated that the kind of by-products is the same as found for the unsupported samples. However, the by-product concentrations in the exit gas are significantly lower. For the impregnated catalysts higher by-product concentrations were determined, in accordance with their lower catalytic activity. The formation of chlorine varied at 650°C from 300 to 1800 vpm depending on the perovskite content.

To compare the catalytic properties of $LaMnO_3$ and $DiMnO_3$ perovskites on zirconia the conversion of 0.1 and 1.0 vol% chloromethane in air was investigated on samples containing 5 mol% perovskite (Fig. 3). In general, the catalytic activity of the $LaMnO_3$-$ZrO_2$ and $DiMnO_3$-$ZrO_2$ catalysts does not differentiate significantly. As expected, the conversion degrees at lower feed concentrations are higher. For a comparison the catalytic behaviour of pure zirconia is shown. Zirconia is catalytically active at reaction temperatures above 400°C. The measured conversion degrees are higher than those in the blank experiments. The formed by-products in the total oxidation of chloromethane on both perovskite catalysts are quite similar. As found on unsupported catalysts the by-product concentration is significantly lower at 0.1 vol% chloromethane in the feed.

In further experiments the fixation of the perovskites on cordierite monoliths were performed by impregnation followed by coating. Under the chosen preparation conditions 7.5 wt.% $LaMnO_3$ and 11.1 wt.% $DiMnO_3$ were fixed on the cordierite ceramic surface. With respect to mole numbers the fixed amounts are quite similar (Table 4).

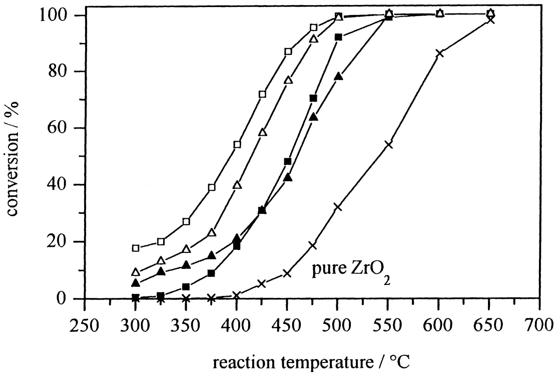

Fig. 3. Conversion of chloromethane on $AMnO_3$-$ZrO_2$ ($LaMnO_3$: □,■; $DiMnO_3$: △,▲) catalysts and on zirconia vs. reaction temperature for different feed concentrations (catalysts prepared by impregnation); 0.1 (open symbols) and 1.0 (full symbols) vol% chloromethane in air; W/F: 43.2 gs $ml^{-1}$.

In Fig. 4 the conversion degrees of methane, chloromethane and dichloromethane on $AMnO_3$ impregnated cordierite monoliths are shown as a function of the reaction temperature. At low reaction temperatures (<450°C) it was found that the reactivity of methane is higher than that of chloromethane and dichloromethane. The complete conversion

Table 4
Average perovskite contents on the cordierite monolithic catalysts in dependence on the preparation method

| | Impregnated | | | Impregnated and coated | | |
|---|---|---|---|---|---|---|
| | wt.% | $\mathrm{kg\,m^{-3}}_{\mathrm{monolith}}$ | $\mathrm{mole\,m^{-3}}_{\mathrm{monolith}}$ | wt.% | $\mathrm{kg\,m^{-3}}_{\mathrm{monolith}}$ | $\mathrm{mole\,m^{-3}}_{\mathrm{monolith}}$ |
| $LaMnO_3$ | 5.3 | 22.4 | 92.6 | 7.5 | 32.2 | 133.1 |
| $DiMnO_3$ | 8.2 | 34.5 | 102.6 | 11.1 | 48.1 | 143.1 |

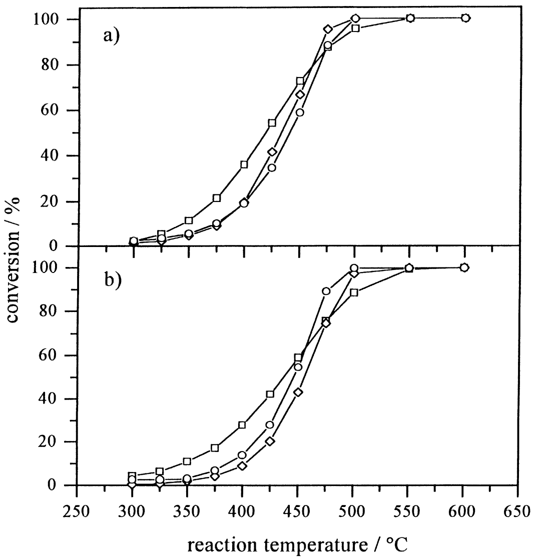

Fig. 4. Conversion of methane (□), chloromethane (◇) and dichloromethane (○) on a) $LaMnO_3$ and b) $DiMnO_3$ impregnated cordierite monoliths in dependence on the reaction temperature (1.0 vol% methane or CHC in air; GHSV = 2300 $h^{-1}$), perovskite contents see Table 4.

Table 5
Concentration of chlorinated by-products in exit gas (vpm) in the oxidation of dichloromethane on $LaMnO_3$ and $DiMnO_3$ impregnated cordierite monoliths[a]

| | Reaction temperature/°C | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 300 | 325 | 350 | 375 | 400 | 425 | 450 | 475 | 500 | 550 |
| *$LaMnO_3$* | | | | | | | | | | |
| $CHCl_3$ | 55 | 95 | 170 | 340 | 700 | 1380 | 2320 | 2580 | 180 | – |
| $CCl_4$ | – | – | – | <10 | 25 | 90 | 320 | 1100 | 2500 | 500 |
| $CHCl{=}CCl_2$ | – | – | – | – | – | – | – | 20 | 55 | 20 |
| *$DiMnO_3$* | | | | | | | | | | |
| $CHCl_3$ | 60 | 110 | 160 | 290 | 560 | 1110 | 2060 | 2300 | 80 | – |
| $CCl_4$ | – | – | – | <10 | 20 | 65 | 260 | 990 | 1740 | 60 |
| $CHCl{=}CCl_2$ | – | – | – | – | – | – | – | 20 | 40 | 30 |

[a] Feed: 1.0 vol% dichloromethane in air; GHSV = 2300 $h^{-1}$.

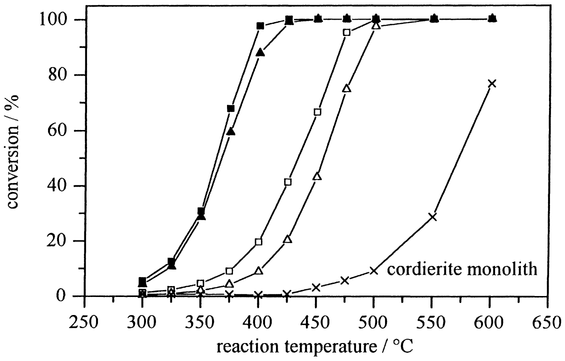

Fig. 5. Influence of the preparation method at the conversion of chloromethane on $AMnO_3$ cordierite monolithic catalysts ($LaMnO_3$: □,■; $DiMnO_3$: △,▲) in dependence on the reaction temperature (preparation method: impregnation (open symbols), impregnation and coating (full symbols)); 1.0 vol% chloromethane in air; GHSV = 2300 $h^{-1}$; perovskite contents see Table 4.

of methane is reached at reaction temperatures above 550°C. The reactivity of chloromethane and dichloromethane does not differentiate significantly. The complete conversion was measured at reaction temperatures of about 500°C. In the low reaction temperature range the $LaMnO_3$ impregnated cordierite monolith is slightly more catalytically active than the $DiMnO_3$ sample.

In Table 5 the by-product concentrations in the exit gas of dichloromethane conversion on $AMnO_3$ impregnated cordierite monoliths are given. Higher chlorinated methanes and traces of trichloroethylene were formed. The higher chlorine content of the dichloromethane molecule in comparison to chloromethane leads to higher by-product concentrations in the exit gas (Tables 5 and 6). The by-product formation on the $DiMnO_3$ catalyst is lower compared with the $LaMnO_3$ sample.

In comparison to impregnated monoliths the coating of monoliths with perovskites leads to catalysts with significant higher catalytic activity (Fig. 5). This is

Table 6
Concentration of chlorinated by-products in exit gas (vpm) in the oxidation of chloromethane on $AMnO_3$ - cordierite monolithic catalysts (according to Fig. 4)[a]

| | Reaction temperature/°C | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 300 | 325 | 350 | 375 | 400 | 425 | 450 | 475 | 500 | 550 |
| *$LaMnO_3$ (impregnated)* | | | | | | | | | | |
| $CH_2Cl_2$ | 40 | 85 | 160 | 310 | 640 | 1240 | 1750 | 1060 | 10 | <10 |
| $CHCl_3$ | – | – | – | – | 25 | 125 | 440 | 1055 | 120 | – |
| $CCl_4$ | – | – | – | – | – | – | 40 | 280 | 980 | 85 |
| $CHCl{=}CCl_2$ | – | – | – | – | – | – | – | <10 | 30 | 10 |
| *$LaMnO_3$ (impregnated and coated)* | | | | | | | | | | |
| $CH_2Cl_2$ | 245 | 520 | 1165 | 1990 | 790 | – | – | – | – | – |
| $CHCl_3$ | <10 | 20 | 95 | 480 | 1020 | – | – | – | – | – |
| $CCl_4$ | – | – | <10 | 50 | 390 | 625 | 140 | 30 | – | – |
| $CHCl{=}CCl_2$ | – | – | – | – | 25 | 20 | – | – | – | – |
| *$DiMnO_3$ (impregnated)* | | | | | | | | | | |
| $CH_2Cl_2$ | 10 | 30 | 70 | 140 | 280 | 615 | 1260 | 1780 | 800 | <10 |
| $CHCl_3$ | – | – | – | – | 10 | 40 | 190 | 610 | 1050 | – |
| $CCl_4$ | – | – | – | – | – | – | 10 | 70 | 330 | 85 |
| $CHCl{=}CCl_2$ | – | – | – | – | – | – | – | – | 25 | 25 |
| *$DiMnO_3$ (impregnated and coated)* | | | | | | | | | | |
| $CH_2Cl_2$ | 290 | 540 | 1200 | 2000 | 860 | 20 | – | – | – | – |
| $CHCl_3$ | 20 | 30 | 70 | 450 | 980 | 10 | – | – | – | – |
| $CCl_4$ | – | – | 10 | 60 | 410 | 645 | 120 | 20 | – | – |
| $CHCl{=}CCl_2$ | – | – | – | – | 25 | 30 | – | – | – | |

[a] Feed: 1.0 vol% chloromethane in air, GHSV = 2300 $h^{-1}$.

caused by the higher perovskite content. On the other hand it is supposed that structure differences between the perovskites formed after impregnation and formed after coating influence the catalytic activity. It is assumed that the crystallinity of the coated perovskites is higher than that of perovskites prepared by impregnation [20].

The kind of the formed by-products is the same for the impregnated and coated monolithic catalysts. The coating of the monoliths with perovskites leads to a significant diminishing of the by-product concentrations at reaction temperatures above 400°C. This is in agreement with their higher catalytic activity.

## 4. Conclusions

The catalytic behaviour of supported and unsupported perovskite-type oxide catalysts $AMnO_3$ with Didym or La in A position is quite similar in the total oxidation of CHC. Interactions of the reaction products with the perovskites decrease their specific surface areas. Within the investigated reaction time no remarkable destruction of the $AMnO_3$ perovskite structure was observed.

Porous zirconia as support enhances the catalytic activity of $AMnO_3$ perovskites in the total oxidation of chloromethane. A maximum of the catalytic activity was found for catalysts with a perovskite content of 5 mol% prepared by precipitation-deposition. The obtained results are a reference for the influence of the crystallinity of the perovskite component on the catalytic activity in the destruction of CHC.

$AMnO_3$ perovskites supported on cordierite monoliths are catalytically active and mechanically stable. The preparation method (impregnation and coating) influences the catalytic activity of the samples in the total oxidation of chloromethane. Coated monoliths exhibit a higher catalytic activity because of their higher perovskite content. The reactivity of chloro- and dichloromethane in the oxidation reaction on $AMnO_3$ cordierite monoliths is comparable.

By-products (higher chlorinated hydrocarbons, lower molecular coupling products) were formed at low reaction temperatures. Polychlorinated dibenzodioxines and dibenzofuranes, carbon monoxide and phosgene could not be identified. The amounts of formed by-products on perovskites supported on zirconia by precipitation-deposition and on coated monoliths are significant lower compared with those on unsupported perovskites.

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