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Catalytic oxidation of 1,2-dichlorobenzene over ABO_3-type perovskites

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Abstract

Several ABO_3-type perovskite oxides (A = La, Y, Nd or Gd; B = Fe, Mn, Cr or Co) have been investigated as catalysts for the oxidation of 1,2-dichlorobenzene (*o*-DCB), a model compound for the highly toxic polychlorinated dibenzodioxins. Initial transient and steady state activity measurements were conducted with all catalysts in the absence and presence of water. Perovskites containing Cr in the B-site were more active than perovskites containing other transition metals, with $YCrO_3$ being the most active catalyst among the different systems studied. Furthermore, $YCrO_3$ did not show any loss of its initial activity after several hours on stream. Other perovskites lost 10–20% of their initial activity within the first 5–10 h on stream. This loss was associated with a corresponding loss in BET surface area. With the exception of $LaCoO_3$, all perovskites retained their crystalline structure upon exposure to *o*-DCB under reaction conditions. $LaCoO_3$ was converted to LaOCl and Co_3O_4. The presence of water appeared to enhance the catalytic activity of some perovskites. This effect can be attributed to a faster removal of Cl^- ions from the catalyst surface via their reaction with water.

Keywords: Dichlorobenzene; Oxidation; PCDD/ PCDF; Perovskites

1. Introduction

In recent years, the incineration of municipal and medical waste has become the preferred method for waste treatment in large residential areas. The flue gas of such processes contains small amounts of several air pollutants, including NO_x, SO_x, particulate matter, and traces of chlorinated volatile organic compounds (Cl-VOCs). Highly toxic polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) are included among these Cl-VOCs. The control of the emissions of PCDDs and PCDFs is critical due to the major health problems associated with exposure to these compounds [1]. Hence, stringent environmental regulations are in place in several countries limiting PCDD/PCDF emissions. In Germany for example, the "17. BImSchVA vom 23.11.1990, BGB1 I, 2545" has placed a limiting value of 0.1 ng I-TEQ/Nm^3 for PCDD/PCDF emissions from municipal and hazardous waste incinerators [2]. Similar limits have been in effect in several European countries since the early 1990s and in Japan since 1997 [3,4].

The preferred method of destruction of PCDD/PCDFs is their catalytic oxidation to carbon dioxide, HCl and water. In fact, this approach is used commercially, since V_2O_5/TiO_2-based catalysts were found to be active in field measurements [5,6]. Anticipation

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of a wide spread use of such systems has led to recent efforts aiming to understanding the surface chemistry taking place during the catalytic destruction of chlorinated aromatics, and eventually the design of improved catalysts [2,7–16]. Model compounds have been used in the majority of these studies due to the highly toxicity of PCDD/PCDFs. Chlorobenzenes, and in particular, 1,2-dichlorobenzene (*o*-DCB), have been frequently used [7,11,13,17,19] because of their structural similarity to 2,3,7,8-tetrachloro-dibenzodioxin (TCDD) which is the most toxic among the different PCDDs.

Perovskite-type mixed metal oxides with the general formula ABO_3 (in which A is a rare earth or alkali earth ion and B is 3d, 4d or 5d transition metal ion), have been recently attracting attention as oxidation catalysts [19–21]. Important properties of perovskites for their catalytic applications include the stability of mixed and unusual valence states of the transition metal ions in their structure, the presence of defect sites, and the high mobility of oxygen ions. Substitution in both the A and B sites changes the composition and symmetry of the perovskite and can affect the stability of different valence states of the metal cations. Furthermore, substitution with ions of a different valence can create cation or anion vacancies, which have a major influence on the catalytic behavior of these materials [21–23]. Finally, when compared to noble metal-based catalysts, perovskites have better thermal stability, are less sensitive towards poisoning by sulfur, phosphorus and halogens, and are less expensive [22].

The goal of this study is to explore the activity of perovskite-type catalysts for the oxidation of chlorinated aromatics. Perovskite-type oxides have been examined for the oxidation of chlorinated aliphatic compounds [22,24–28]. To the best of our knowledge however, only one other study is available regarding the activity of different ABO_3-type perovskites ($A =$ La; $B =$ Co, Mn) for the oxidation of chlorobenzene [18]. Our work focuses on the comparison of different ABO_3-type perovskites and the effect of the nature of the A and B cations on catalytic activity and stability for the oxidation of *o*-DCB. Activity measurements were conducted in a plug flow microreactor. All catalysts were also characterized by means of X-ray diffraction and BET surface area measurements before and after exposure to reaction conditions.

2. Experimental

2.1. Materials

ABO_3-type perovskites containing La, Y, Nd or Gd in the A-site and Co, Fe, Mn or Cr in the B-site were used in this study. All perovskites were synthesized via the amorphous citrate precursor method [29]. Stoichiometric amounts of aqueous solutions of the nitrates of the corresponding metals were mixed with an aqueous solution of citric acid, so that the ratio of the total moles of metal to the moles of citric acid was equal to one. The resulting aqueous solution was stirred and heated to approximately 80°C to obtain a gel, which was then dried for 20 h in a vacuum oven at 80°C. The resulting materials were then calcined in air at elevated temperatures to yield the desired perovskite structures. As shown in Table 1, the calcination temperatures and times varied between 650 and 850°C and

Table 1
Calcination characteristics and BET surface areas for the different perovskites used

Perovskite	Calcination time (h)	Calcination temperature (°C)	BET surface area (fresh catalysts) (m^2/g)	BET surface area (used catalysts) (m^2/g)
$LaCoO_3$	2	650	12	6
$LaFeO_3$	2	650	19	11
$LaMnO_3$	2	650	35	22
$LaCrO_3$	6	650	8	6
$YFeO_3$	3	750	14	17
$YMnO_3$	12	850	15	14
$YCrO_3$	5	750	9	9
$NdCrO_3$	5	750	5	5
$GdCrO_3$	5	750	5	6

2 and 12 h respectively, depending on the perovskite synthesized. The minimal temperature and calcination time combination yielding the perovskite structure was chosen in each case, so that the surface areas of the resulting perovskite materials were maximized.

2.2. Characterization

X-ray diffraction (XRD) patterns of the perovskite samples were collected before and after the use of these samples in kinetic experiments, with a Rigaku D/max-B diffractometer equipped with a nickel-filtered Cu Kα radiation source ($\lambda = 1.5406$ A). These XRD patterns were analyzed with a commercial JPDSS database by ICDD, and indicated the formation of a crystalline perovskite phase in all fresh samples. BET surface area measurements of fresh and used perovskites were conducted with a Pulse Chemisorb 2000 (Micromertrics) analyzer. As shown in Table 1 surface areas in the range of 5–35 m^2/g were obtained with the fresh samples, which are comparable to the values reported in the literature for materials prepared by the same method [19].

2.3. Reactor studies

Activity measurements were conducted in a quartz, single-pass, fixed bed reactor. Each run utilized approximately 250 mg of catalyst in the form of 80 to 120 mesh (125–177 μm) particles. Prior to each experiment, catalysts were pretreated in pure oxygen for 2 h at 500°C. A K-type thermocouple was placed into the catalyst bed to monitor the reaction temperature. The reaction mixture contained approximately 600 ppmv *o*-DCB, introduced to the reactor system by the passage of a He stream through an *o*-DCB saturator, 10% O_2 and balance He. The volumetric flow rate through the catalyst bed was held constant at 222 standard cm^3/min. A water saturator was also added to the system during the experiments conducted in the presence of water. The concentration of *o*-DCB in the reactor inlet and exit streams was determined online with a gas chromatograph (SRI 8610) equipped with a 1/8″ packed silica-gel column (230°C) and a flame ionization detector.

Experiments carried out with a diluted catalyst bed (with quartz particles of the same mesh size) and with catalyst particles of different sizes demonstrated the absence of any mass or heat transfer limitations in our reactor system.

3. Results and discussion

3.1. Effect of the B-site cation

The effect of the nature of the transition metal occupying the B site on the activity of La–containing perovskites was examined first. Results of initial transient measurements conducted at 600°C in the presence and absence of water are shown in Fig. 1. All samples appear to undergo an initial deactivation period before a steady state is established. A 10–20% loss of the initial activity was observed during this period for the $LaFeO_3$ and $LaCrO_3$ catalysts. A steady state was established in these cases within the first 5–10 h.

On the contrary, a more prolonged deactivation period (20 h) was observed in the case of $LaCoO_3$ (especially in the presence of water). This catalyst lost more than 50% of its initial activity during this time. XRD patterns indicate that the $LaCoO_3$ perovskite structure is destroyed during this period and two new phases consisting of lanthanum oxychloride (LaOCl) and cobalt oxide (Co_3O_4) are formed (Fig. 2). The presence of water apparently slows down this transformation (presumably by reacting with the surface Cl^-), but eventually the same steady state is reached. The break down of $LaCoO_3$ to LaOCl and Co_3O_4 was also observed by Kießling et al. [28] during the oxidation of 1,2-dichloroethane. The observed steady state activity of this material is probably due to the presence of cobalt oxide, since previous studies have shown that supported cobalt oxide catalysts are active for the oxidation of *o*-DCB under similar conditions [9].

No signs of any other phase changes were observed in the XRD patterns of the other perovskites. Nevertheless, BET surface area measurements of used samples (Table 1) indicate a significant loss of surface area for all $LaMO_3$ catalysts as a result of exposure to reaction conditions. This loss of surface area may be in part responsible for the observed initial deactivation. We should point out, that the loss of surface area is associated with exposure to *o*-DCB and not simply a prolonged calcination at the reaction temperatures.

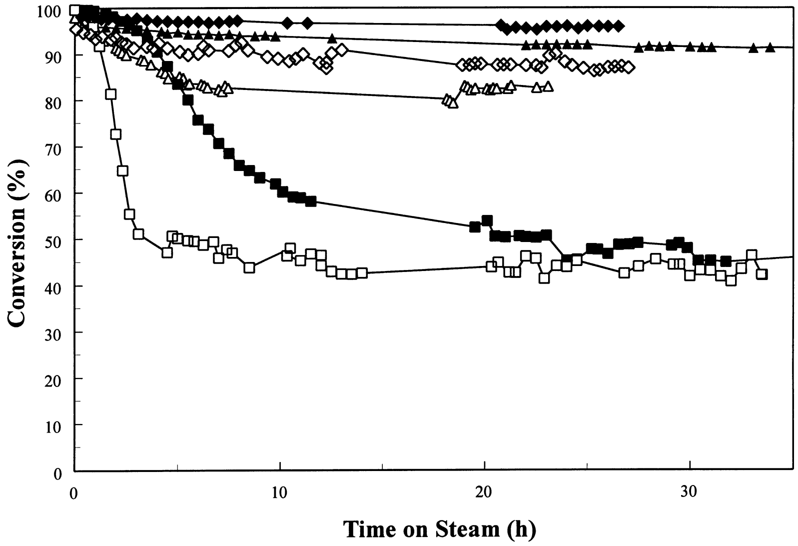

Fig. 1. Initial transient behavior of $LaMO_3$ systems in the presence and absence of water: (◆, ◇) $LaFeO_3$, (▲, △) $LaCrO_3$, (■, □) $LaCoO_3$ (open symbols: 600 ppm *o*-DCB, 10% O_2; filled symbols: 600 ppm *o*-DCB, 10% O_2, 1% H_2O).

The conversion of *o*-DCB over different $LaMO_3$ (M = Fe, Mn, Cr, Co) perovskites is shown as a function of temperature in Fig. 3. These data were collected following the initial deactivation period described above, and represent the long-term steady state activity of these catalysts. In many cases each point represents an average value of several measurements. Excellent reproducibility (<5% variation) was observed during these multiple measurements. All perovskites studied were found to be active for the oxidation of *o*-DCB; their activity at 500°C decreased in the order of $LaCrO_3 > LaMnO_3 > LaFeO_3 > LaCoO_3$. The observed order is in agreement with results obtained by Krishnamoorthy et al. [9] for the same reaction and transition metals in their common oxide form (i.e. Fe_2O_3, Cr_2O_3 and Co_3O_4) supported on Al_2O_3.

Similar steady state activities were obtained both in the presence and absence of water. However, a small promoting effect by water was noted for $LaCrO_3$ and $LaFeO_3$. Water is present in significant amounts in exhaust streams from incinerators that contain PCDD/PCDFs. A similar promoting effect has been also observed by Krishnamoorthy et al. [9] for the oxidation of *o*-DCB over Co_3O_4/TiO_2. In this case the effect of water was attributed to an increased rate of removal of surface chlorine ions from the catalyst (i.e. $Cl^- + H_2O \Leftrightarrow HCl + OH^-$). Similarly, Shaw et al. [30] have also reported that the presence of water enhances the rate of the oxidation of trichloroethylene over Pt, Pd and MnO_2 catalysts.

3.2. *Effect of the A-site cation*

The effect of the A-site cation was examined next. First, a series of YMO_3 catalysts (M = Cr, Fe, Mn) was prepared and the activity results were compared to those obtained with the $LaMO_3$ systems. As can be seen in Fig. 4 replacement of La by Y does not result in significant changes in the activity of the catalysts containing Fe and Mn in the B-site. These findings are in agreement with the results of earlier studies on the oxidation of methanol and propane over perovskite catalysts [21], which concluded that the role of the A-site cation is secondary, as long as a trivalent cation is used. On the contrary, replacement of La by Y in the Cr-containing perovskites resulted in a significant increase in activity for the oxidation of *o*-DCB. Furthermore, initial transient measurements indicate that no significant deactivation takes place in this system as the result of exposure to reaction conditions. The activities of other Cr-containing perovskites with trivalent rare earth cations in the A-site were found to be intermediate to these of $LaCrO_3$ and $YCrO_3$ (Fig. 5).

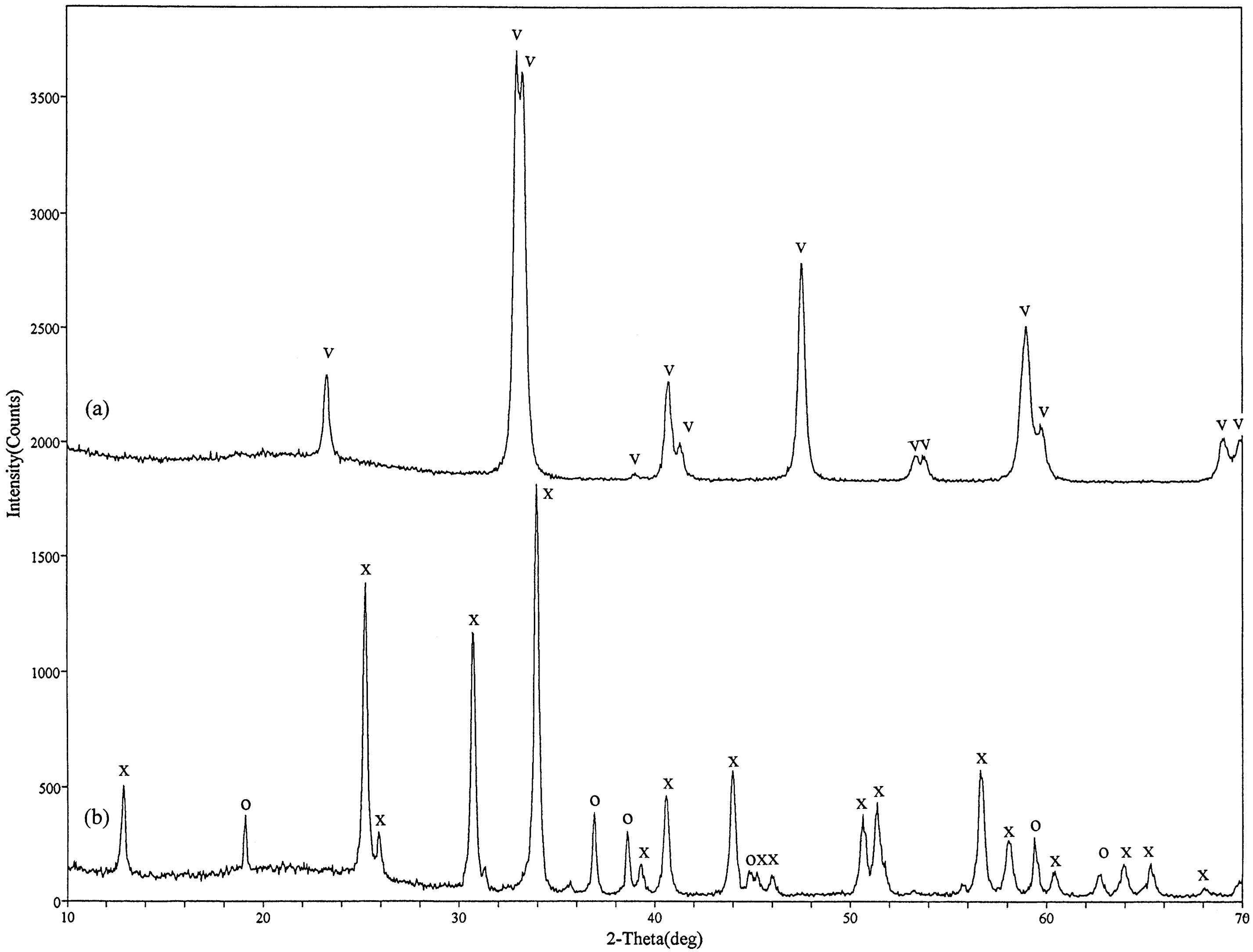

Fig. 2. XRD patterns of $LaCoO_3$ (a) before and (b) after exposure to reaction conditions for 30 h (v: $LaCoO_3$, (×): LaOCl, (○): Co_3O_4).

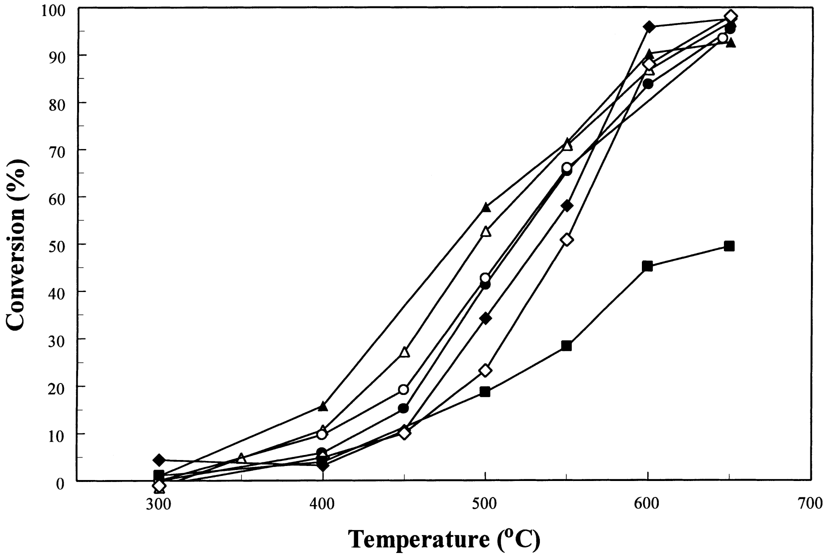

Fig. 3. Steady-state *o*-DCB conversion as a function of temperature in the presence and absence of water: (▲, △) $LaCrO_3$, (●, ○) $LaMnO_3$, (◆, ◇) $LaFeO_3$, (■) $LaCoO_3$ (open symbols: 600 ppm *o*-DCB, 10% O_2; filled symbols: 600 ppm *o*-DCB, 10% O_2, 1% H_2O).

We should finally point out that no loss in BET surface area was observed with the perovskites containing Y, Gd or Nd in the A-site after exposure to the reacting gas mixture (Table 1), contrary to what was observed with the $LaMO_3$ systems. These results may suggest that the interaction of La with Cl is responsible for the observed losses in surface area, and that the presence of other rare earth ions in the A-site stabilizes the perovskite structure in the presence of Cl.

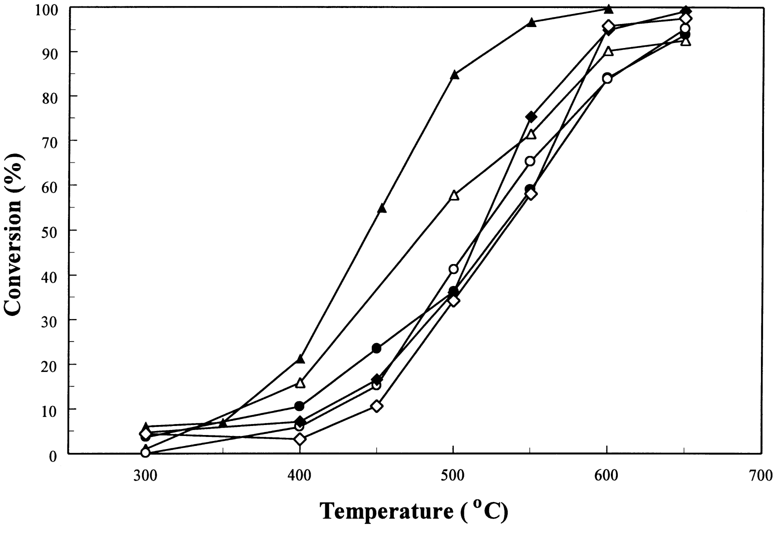

Fig. 4. Steady-state *o*-DCB conversion as a function of temperature for different catalysts tested: (▲) $YCrO_3$, (△) $LaCrO_3$, (●) $YMnO_3$, (○) $LaMnO_3$, (◆) $YFeO_3$ and (◇) $LaFeO_3$ (600 ppm *o*-DCB, 10% O_2, 1% H_2O).

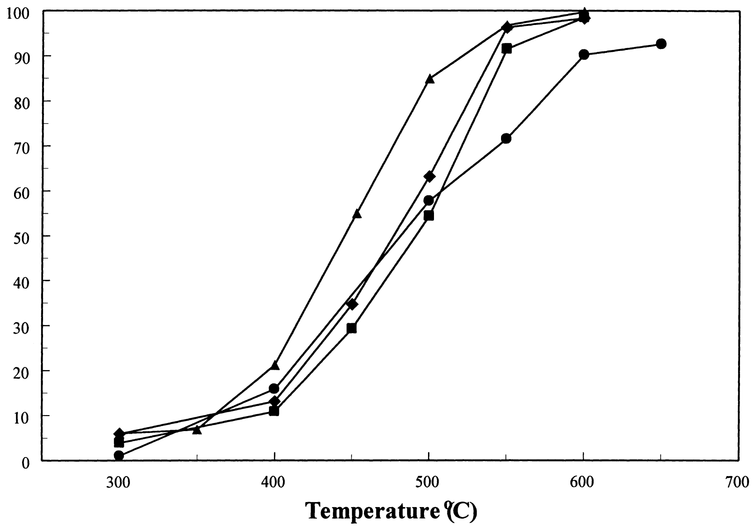

Fig. 5. Steady-state *o*-DCB conversion as a function of temperature for different catalysts tested: (▲) $YCrO_3$, (◆) $GdCrO_3$, (■) $NdCrO_3$, (●) $LaCrO_3$ (600 ppm *o*-DCB, 10% O_2, 1% H_2O).

3.3. Reaction by-products

In addition to *o*-DCB, the online GC analysis indicated the presence of trace amounts of an unknown organic by-product in the reactor exit stream. The concentration of this species reached a maximum value at approximately 550°C in all cases, suggesting that it is further oxidized to CO and CO_2 at higher temperatures. In an effort to identify the nature of this species, samples of the exit gas stream were collected in a trap maintained at 0°C. The collected liquid was then extracted in methylene chloride and analyzed by means of gas chromatography/ mass spectrometry. The results indicate the presence of a mixture of tri- and tetrachlorinated phenols consistent with the higher retention times observed during the on-line GC analysis. We should point out, that formation of these phenols was observed with all catalysts tested, with the exception of $ACrO_3$ (A = La, Y, Nd, Gd) systems in the presence of water.

The formation of higher chlorinated products has also been reported by other research groups working in the same area. Van den Brink et al. [11] for example, reported the formation of polychlorinated benzenes (Cl = 2–6) as by-products of the oxidation of chlorobenzene over Pt/Al_2O_3. In agreement with our results, they reported that the concentration of these species exhibited a maximum at approximately 400–450°C and that the addition of water to the reaction mixture significantly decreased their formation. Kießling et al [22,28] also observed the formation of higher chlorinated compounds during the oxidation of chloromethane, dichloromethane and 1,2-dichloroethane over perovskite catalysts. They suggested that the formation of these compounds takes place by insertion of chlorine into reactants and/or intermediates on the catalyst surface. Depending on the compound studied, they also observed a maximum in the concentration of these species in the 450–600°C temperature range. From a practical standpoint however, the formation of CO or any other partial oxidation by-product does not represent a problem in the case of the oxidation of PCDD/PCDFs, due to the very low concentration of these compounds in the flue gas of the incinerators (ppb level) and their extremely high toxicity equivalence.

4. Conclusions

Several different ABO_3-type perovskites (A = La, Y, Gd or Nd; B = Cr, Co, Fe or Mn) were prepared via the citrate method, and tested as catalysts for the oxidation of *o*-DCB. Initial transient measurements were conducted over these catalysts at 600°C. The results indicate the presence of an initial deactivation period for most of these systems, which is associated with an observed loss of BET surface area. The most dramatic differences were observed with $LaCoO_3$, which loses more than 50% of its initial activity and breaks down to LaOCl and Co_3O_4. All other perovskites lost less than 15% of their initial activity and appeared to retain their crystalline perovskite structure. A steady state was eventually established in all cases after 5–20 h on stream.

Steady state activity measurements conducted both in the presence and absence of water indicate that the Cr-containing perovskites are the most active ones, in agreement with previous reports regarding the corresponding supported metal oxide systems. Replacement of La in the A-site with other rare earth trivalent cations resulted in a stabilization of the surface areas and, in some cases, an improvement of catalytic activity. The $YCrO_3$ catalyst was significantly more active among the different $ACrO_3$ systems. Finally, the presence of water in the reacting gas mixture enhanced the catalytic activity in some cases. This can be attributed to a faster removal of surface Cl^- ions from the catalyst.

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References

[1] J. Johnson, Environ. Sci. Tech. 29 (1995) A24.
[2] R. Weber, T. Sakurai, H. Hagenmeier, Appl. Catal. B 20 (1999) 249.
[3] Guideline for Controlling PCDDs/DFs in MSW Management, the Advisory Committee for Controlling PCDDs/PCDFs in MSW Management, 1997.
[4] M. Hiraoka, S. Sakai, T. Sakagawa, Y. Hata, Organohalogen Compounds 31 (1997) 446.
[5] R. Boos, R. Budin, H. Hartl, M. Stock, F. Wurst, Chemosphere 25 (1992) 375.
[6] K.B. Carlsson, Chemosphere 25 (1992) 135.
[7] S. Krishnamoorthy, J.P. Baker, M.D. Amridis, Catal. Today 40 (1998) 39.
[8] S. Krishnamoorthy, M.D. Amiridis, Catal. Today 51 (1999) 3.
[9] S. Krishnamoorthy, J.A. Rivas, M.D. Amiridis, J. Catal. 193 (2000) 264.
[10] R.W. van den Brink, P. Mulder, R. Louw, G. Singuin, C. Petit, J.P. Hindermann, J. Catal. 180 (1998) 153.
[11] R.W. van den Brink, R. Louw, P. Mulder, Appl. Catal. B 16 (1998) 219.
[12] R.W. van den Brink, P. Mulder, R. Louw, Catal. Today 54 (1999) 101.
[13] I.M. Freidel, A.C. Frost, K.J. Herbert, F.J. Meyer, J.C. Summers, Catal. Today 17 (1993) 367.
[14] R.W. van den Brink, M. Krzan, M.M.R. Feijen-Jeurissen, R. Louw, P. Mulder, Appl. Catal. B 24 (2000) 255.
[15] G. Busca, M. Baldi, C. Pistarino, J.M.G. Amores, V.S. Escribano, E. Finocchio, G. Romezzano, F. Bregani, G.P. Toledo, Catal. Today 53 (1999) 525.
[16] J. Jones, J.R.H. Ross, Catal. Today 35 (1-2) (1997) 97.
[17] G.R. Lester, R.F. Renneke, K.J. Herbert, in: Proceedings of the Annual Meeting of the Air and Waste Management Association. Kansas City, MO, 1992.
[18] G. Sinquin, J.P. Hindermann, C. Petit, A. Kiennemann, Catal. Today 54 (1999) 107.
[19] E.A. Lombardo, M.A. Ulla, Res. Chem. Intermed. 24 (1998) 581.
[20] V.R. Choudhari, B.S. Uphade, A.A. Belhekar, J. Catal. 163 (1996) 312.
[21] T. Nitadori, T. Ichiki, M. Misono, Bull. Chem. Soc. Jpn. 61 (1988) 621.
[22] R. Schneider, D. Kiessling, P. Kraak, M. Haftendorn, G. Wendt, Chemische Technik 47 (1995) 4.
[23] K. Song, H.X. Cui, S.D. Kim, S. Kang, Catal. Today 47 (1999) 155.
[24] K. Stephan, M. Hackenberger, D. Kiessling, G. Wendt, Catal. Today 54 (1999) 23.
[25] R. Schneider, D. Kiessling, R. Herzschuh, G. Wendt, React. Kinet. Catal. Lett. 61 (2) (1997) 245.
[26] M. Hackenberger, K. Stephan, D. Kiessling, W. Schmitz, G. Wendt, Solid State Ionics 101–103 (1997) 1195.
[27] R. Schneider, D. Kiessling, G. Wendt, W. Burckhardt, G. Winterstein, Catal. Today 47 (1999) 429.
[28] D. Kießling, R. Schneider, P. Kraak, M. Haftendorn, G. Wendt, Appl. Catal. B 19 (1998) 143.
[29] H.M. Zhang, Y. Teraoka, N. Yamazoe, Chem. Lett. 4 (1987) 665.
[30] H. Shaw, Y. Wang, R.J. Furrauto, ACS Symp. Ser. 45 (1992) 125.