CATALYTIC DESTRUCTION OF HAZARDOUS HALOGENATED ORGANIC CHEMICALS

George R. Lester
Allied-Signal Engineered Materials Research Center
Des Plaines, Illinois

As Presented at the Air & Waste Management Association
82nd Annual Meeting & Exposition
June 25 — 30, 1989
Anaheim, California
INTRODUCTION

Catalytic incineration is widely used for the destruction of hazardous volatile organic compounds found in air emissions and other gas streams which are vented from a variety of industrial processes. Such streams include those vented from processes for the manufacture of organic chemicals and polymers, vent air from operations in which volatile organic solvents are used for cleaning and degreasing purposes in metal processing, machining and finishing, and the vent or exhaust air from air stripping process units which are used to clean groundwater or soil which has been contaminated with hazardous volatile organic chemicals and solvents. Because catalytic incineration is able to operate at significantly lower temperatures and with considerably lower residence times than the thermal incineration alternative, it offers very important cost incentives in terms of much lower costs for supplemental fuel and in the use of smaller reactors made of less expensive materials of construction.

Many of the streams which must be purified contain significant amounts of halogenated organics, such as the polychlorinated ethanes and ethylenes vented in the manufacture of vinyl chloride monomer or released in their use as industrial and/or military solvents, or the polychlorinated and/or fluorinated organics in the vent air from groundwater and/or soil remediation processes. However, the precious metal catalysts used in the conventional catalytic incinerator are severely inhibited in their performance by the halogen atoms in these compounds, and this desirable process cannot generally be used with such catalysts for these applications. At least two catalytic processes have been used to purify such streams, but both utilize fluidized beds of (probably non-noble metal) catalyst particles. One of these units has been estimated to incinerate over 20 million pounds per year of chlorinated wastes from a vinyl chloride monomer plant.

Fluidized bed incineration processes in which the catalyst performance depends on the continuous attrition of the halogen-laden external surface of the catalyst particles have many unattractive features, including the effort required for trapping, collecting, and disposing of the fine particulate released from the reactor.

The objective of this study was to develop an active, stable, poison-resistant catalyst that could be used in the form of a monolithic honeycomb or as a fixed bed of granules, extrudate, spheres, etc., for the complete destruction of hazardous volatile halogenated organic compounds.

EXPERIMENTAL

Experimental reaction apparatus

The schematic flow diagram of the test apparatus is shown in Figure 1. Carefully metered gas streams are mixed after some of the streams have been saturated with water and/or liquid organics in temperature-controlled saturators. The blended reactor feed can be analyzed before or after it has passed through the reactor. The analytical capabilities include specific gas detection tubes for "spot" analyses for such possible
products or by-products as phosgene, chlorine (Cl₂), vinyl chloride monomer, etc.; collection or trapping of gas samples for separate GC analysis; scrubbing the gas with prepared analytical solutions for subsequent titration, ion chromatography, or other analytical procedures; and determination and continuous analysis for hydrocarbon and/or halogenated hydrocarbons by a heated flame ionization analyzer (Beckman 400) and for CO₂ and CO by appropriate Beckman non-dispersive infrared analyzers. The flame ionization detector (FID) was calibrated for each halohydrocarbon with the feed stream by-passing the reactor on the assumption that the published vapor pressure of the halohydrocarbon was correct and that saturation and mixing were proper. This assumption was tested, and corrected if necessary, by the CO₂ and CO analysis of the product gas at a condition when complete destruction of the compound was occurring, based on NDIR, CO₂, and CO analyzers. If necessary, confirmatory analysis was done by gas detector tubes and/or supplemental GC analysis.

The quartz test reactor is shown in Figure 2. The feed blend is preheated by the furnace and the reactor effluent as it flows past the catalyst bed in an annular section; flow then reverses and continues through the catalyst monolith or the bed of catalyst extrudate or granules. The catalyst bed section was normally 7/8” diameter and 1” long; the fixed beds of extruded particles were supported by a short section of uncatalyzed 400 cells/in² ceramic (cordierite) monolith. The catalyst bed length and/or gas flow rate (normally 2.5 liters [STP] per minute) were adjusted as needed to obtain space velocities other than the usual 15,000 hr⁻¹ GHSV (STP).

Normal test procedure

After the feed blend had been analyzed through the reactor bypass, the catalyst was heated to 400°C in the flowing feed blend. If feed destruction was less than 99% at that condition, the temperature was increased to achieve 99% destruction. The temperature was then cooled down at a rate of about 4°C/minute, while the degree of destruction was continuously monitored. Because of the reactor design, there were normally only small temperature gradients (<5°C) across the catalyst bed. For consistency, inlet temperatures have been used for all of the data presented here.

Catalyst

The proprietary halohydrocarbon destruction catalyst (HDC) was prepared in the form of a coated monolith and also as extruded (1/16” diameter x 1/16” long) pellets. The monolithic support was the 400 cells/in² Corning cordierite ceramic (square cells, 8mil wall thickness) used in conventional automotive catalytic converters.

Products of catalytic destruction

Complete catalytic destruction of the feed halogenated organics minimizes the possibilities of production of hazardous products of incomplete combustion (PICs) such as carbon monoxide (CO). It is also important that sufficient hydrogen be present in the feed, as organic matter and/or water vapor, to minimize production of chlorine gas
Figure 1. Schematic diagram of laboratory activity test apparatus.

Figure 2. Diagram of quartz activity test reactor.
(Cl₂) rather than the desired hydrogen chloride (HCl). In the occasional measurements of HCl and Cl₂ yield, the Cl₂ was always below 20 volume ppm in the effluent or less than 6 percent of the total inorganic chloride produced.

RESULTS

Relevant prior studies

Although a large number of base and noble metal catalysts have been evaluated for the destruction of halogenated volatile organic compounds, chromia-aluminas (typically 12-25 w.% chromia calculated as Cr₂O₃) seem to have been used most broadly and successfully.

Manning studied the kinetics of destruction of methylene chloride (CH₂Cl₂) and several polychlorinated ethylenes in moistened air with a recycle reactor containing a commercially available 12 w.% Cr₂O₃ on Al₂O₃ (0.40 cm x 0.40 cm pellets, Strem 24-0200). He concluded that the reaction was first order in the chlorohydrocarbon (except half order for trichloroethylene [C₂HCl₃]) and between zero and first order in oxygen. The reaction was slightly inhibited by water for all of the chlorohydrocarbons except perchloroethylene (C₂Cl₄). However, the presence of water improved the catalyst stability; it was suggested that the water inhibited the loss of Cr from the reactor, which presumably occurred as a result of the reaction of Cr₂O₃ with the chlorohydrocarbon (or with the oxidation product Cl₂) to produce the volatile red oxychloride, CrO₂Cl₂.

Weldon and Sengar reported a kinetic study of the destruction of methylchloride (CH₃Cl) with a powder (1 mm diameter) crushed from another commercially available Cr₂O₃-Al₂O₃ (1/8” Pellets, 19 w.% as Cr₂O₃, Harshaw). They also concluded that the reaction was first order (or perhaps non-linear second order) in the chlorohydrocarbon and zero order in O₂. Because their reaction gases were dry (except for product H₂O), they found selectivity to Cl₂ (relative to HCl) of 3-7 percent; this was significantly less than would correspond to the full Deacon equilibrium (4 HCl + O₂ → 2Cl₂ + 2H₂O), which would be in the range of 15-50 percent for their conditions. By contrast, Laidig had found selectivities of 19-42 percent Cl₂ using copper-based catalysts. The difference probably reflects the significant difference in the relative efficacy of Cr and Cu for the Deacon reaction.

The research group at the University of Bath which is seeking to develop a process for the catalytic combustion of polychlorinated biphenyls has measured the efficiency of destruction of 1,2,4-trichlorobenzene with packed beds of either 20 w.% Cr₂O₃-Al₂O₃ or 0.3 w.% Pt-Al₂O₃ in 3.2 mm cylindrical pellets at 500-800°C at air:fuel stoichiometry and with 25% excess air. At least 800°C was required to achieve 99% conversion with either catalyst, but the Cr₂O₃-Al₂O₃ was more active in the range of 500-800°C.
Figure 3. Comparison of HDC and Cr-Al monoliths for carbon tetrachloride destruction: 1000 ppmv CCl₄, 10% H₂O, 12% O₂, 15,000 hr⁻¹ GHSV (STP).

Figure 4. Comparison of HDC and Cr-Al monoliths for benzene destruction: 300 ppmv C₆H₆, 2.5% H₂O, 12% O₂, 15,000 hr⁻¹ GHSV (STP).
Chromia-alumina is the only catalyst composition identified in the patent\textsuperscript{15} describing the fluidized-bed catalytic incinerator process of Air Resources, Inc. (ARI) which is reported to be in commercial use for the destruction of chlorinated organics.\textsuperscript{2} The catalyzed bed in this process is fluidized (or, more accurately, agitated by up-flowing air) in an effort to counter the suppression of activity by chlorine (or chloride); it is intended that the continuous abrasion and loss from the reactor of the chlorine-laden outer portion of the catalyst particles will continuously expose unpoisoned particles to the reactants. To this end, the physical properties of the catalyst are adjusted to achieve a loss of about one pound of catalyst per million cubic feet of gas treated, or about 16 mg/m\textsuperscript{3}. A skid-mounted ARI pilot plant, presumably loaded with chromia-alumina spheres per the ARI patent, was used by Radian Corporation under an EPA/Air Force contract in an extensive study of the catalytic destruction of a number of chlorinated organics and hydrocarbons such as might be impurities in the exhaust air from air strippers used to clean up contaminated soil or groundwater.\textsuperscript{16,17} This unit demonstrated 97-99\% destruction of the selected mixtures of chlorinated organics at a space velocity of about 7000 hr\textsuperscript{-1} (STP) and 500°C. The chlorinated organics included vinyl chloride and polychlorinated ethanes and ethylenes.

Although noble metal catalysts have been studied for these reactions\textsuperscript{5,6,9,10,12-14}, their performance has generally been inferior to the chromia-aluminas, presumably because of the inhibition of the rate by the reactant chlorohydrocarbon and/or by the chlorine/chloride products.\textsuperscript{12} For example, a study,\textsuperscript{10} similar otherwise to the chromia-alumina Radian/EPA/AF tests referred to above,\textsuperscript{16,17} with an Engelhard Pt/Pd honeycomb catalyst reported destruction efficiencies of less than 50\% for similar mixtures of chlorinated hydrocarbons which were destroyed at 97-99\% efficiency by the fluidized base metal catalyst.

Results from this study

Comparison of HDC with Cr\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3}. In order to compare the new Allied-Signal halohydrocarbon destruction catalyst (HDC) with the pre-existing catalyst technology, a chromia-alumina catalyst (19.7 w.% Cr\textsubscript{2}O\textsubscript{3} on Al\textsubscript{2}O\textsubscript{3}, 135 m\textsuperscript{2}/g) was obtained from Harshaw Chemical Co. and applied as a washcoat to a Corning 400 cells/in\textsuperscript{2} monolithic catalyst support by a conventional method.\textsuperscript{18} Cores of this catalyst (Cr-Al, 7/8" diameter and 1" long) were tested along side similar size units of the experimental HDC, which were also prepared on the 400 cells/in\textsuperscript{2} Corning cordierite support.

Figure 3 shows conversion-temperature curves for the HDC and Cr-Al monoliths for the destruction of carbon tetrachloride (CCl\textsubscript{4}), tested at 1000 volume ppm at 15,000 hr\textsuperscript{-1} GHSV (STP) in \textsubscript{N}\textsubscript{2} containing 12\% O\textsubscript{2} and 10\% H\textsubscript{2}O. Over 99\% destruction was achieved at about 335°C for the HDC, which was 200°C lower than was required by the Cr-Al reference catalyst. The difference in efficiency is even more pronounced for benzene (Figure 4) which required 225°C for 99\% destruction with the HDC, and 490°C for the Cr-Al catalyst. For this comparison, the benzene level was 300 volume ppm (ppmv), and H\textsubscript{2}O level was 2.5\%. Figure 5 shows that the activity difference is less for toluene, but that the HDC still gives 99\% destruction at a lower temperature than the Cr-Al catalyst by 150°C (230°C vs. 380°C).
Figure 5. Comparison of HDC and Cr-Al monoliths for toluene destruction: 300 ppmv C7H8, 2.5% H2O, 12% O2, 15,000 hr⁻¹ GHSV (STP).

Figure 6. Comparison of HDC and Cr-Al monoliths for 1,2-dichlorobenzene destruction: 30 ppmv C₈H₄Cl₂, 2.5% H₂O, 12% O₂, 15,000 hr⁻¹ GHSV (STP).
The relative efficiency of the two catalysts for 1,2-dichlorobenzene at 30 ppmv is shown in Figure 6. Although this halogenated hydrocarbon is difficult for both catalysts, 99% destruction is achieved by the DHC at 405°C as compared to 500°C for Cr-Al. In this temperature range, the ability to operate at lower temperatures may have a major impact on catalyst stability, beyond the obvious fuel savings which result from the lower temperature operation.

The results shown in these figures for the Cr-Al monolithic catalyst are not unexpected in view of what might have been expected by extrapolation of the literature results for such catalyst in packed beds and fluidized systems. The considerably better performance of the Allied-Signal HDC compared to Cr-Al suggests that it might be usable in fixed bed processes at much lower temperatures than Cr-Al, without the problems associated with fluidized bed operation, including the emission of fine halogen-laden catalyst particulates, or the provision for trapping and collection of such potentially hazardous particulates.

Parametric studies with the Allied-Signal HDC. The effect of water concentration on carbon tetrachloride destruction by the new catalyst is shown in Figure 7, where the destruction efficiency is shown to decrease as the water level is increased from 1.5 to 10 volume percent. This slight inhibition by water in this concentration range probably reflects the competition of the reactant CCl4 with H2O for adsorption at the catalyst site, and indicates the importance of the water concentration, and perhaps the H2O:chlorohydrocarbon ratio in the feed gas.

The stability of the HDC at these operating conditions is also shown in Figure 7. At each water level, the catalysts were operated with the test gas at 375°C for over 48 hours and then retested; the curves for the retest were not distinguishable from the initial tests at either water level. The test at the 10% H2O level was continued through 1600 hours, after which the conversion at 350°C was still above 99%; during the 1600-hour test, the benzene conversion-temperature profile actually shifted slightly to lower temperatures, reflecting an improvement in activity for C6H6 destruction. In a parallel test, it was demonstrated that destruction of CCl4 without water vapor in the feed caused catalyst deactivation and, of course, produced significant amounts of Cb instead of the HCl usually produced. This demonstrates the importance of water vapor in stabilizing the catalyst performance, and for producing the desired HCl rather than Cb.

Figure 8 includes plots of the destruction of 1,1,2-trichloroethane (C8HC-CH2Cl) at 450 ppmv and at two gas flow rates. At the 99% conversion level, operation at the lower flow rate (7500 hr⁻¹ GHSV [STP]) requires only 400°C instead of the 440°C required at the higher rate.

A somewhat negative order of the reaction with respect to the 1,1,2-trichloroethane is indicated in Figure 9. The nine-fold increase in halogenated organic from 50 to 450 ppm increases the temperature required for 99% conversion from 360°C to 400°C required at the higher rate.

The new halohydrocarbon destruction catalyst can also be prepared as an extrudate, granules, or in pellet forms for use in fixed bed reactors. Figure 10 shows results for CCl4 with the catalyst in the form of 1/16" extrudates at two different gas flow rates;
Figure 7. Destruction of carbon tetrachloride over monolithic HDC at 1.5 and 10% H₂O levels: 1000 ppmv CCl₄ in air at 15,000 hr⁻¹ GHSV (STP), 1.5 or 10 volume % H₂O.

Figure 8. Destruction of 1,1,2-trichloroethane over monolithic HDC at two gas throughput rates: 1.5% H₂O in air at 7500 and 15,000 hr⁻¹ GHSV (STP), 450 ppmv C₂H₅Cl₃.
Figure 9. Destruction of 1,1,2-trichloroethane over monolithic HDC at two C₂H₃Cl₃ concentrations: 1.5% H₂O in air at 7500 hr⁻¹ GHSV (STP).

Figure 10. Destruction of carbon tetrachloride by bed of 1/16-inch HDC extrudate at two space velocities and monolithic HDC at 15,000 hr⁻¹ GHSV (STP): 1.5% H₂O in air, 1000 ppmv CCl₄.
the plot for the 400 cells/in² monolithic catalyst is also shown for comparison. It is obvious that the extrudate bed gives somewhat better performance than the monolith at the same flow rate, but the back pressure is, of course, much greater in the extrudate bed.

The relative ease of destruction of the chloromethanes by the HDC is shown in Figure 11, at concentrations of 500-900 ppmv. The ease of destruction as shown increases monotonically from CH₂Cl (most difficult) to CCl₄ (easiest) as the number of chlorine atoms increases; this in spite of an increasing actual Cl atom concentration across the series from 600 ppm (Cl atom) for CH₂Cl to 3,600 ppm (Cl atom) for CCl₄. The observed order of stability is in the same order as the lowest bond dissociation energies (LBDE's²⁹), but is opposite to that found by Bond and Sadeghi for destruction of the polychloromethanes with several Pt-Al₂O₃ catalysts.¹³ The LBDE's and the temperatures required to achieve 99% destruction with the HDC catalyst are tabulated here, along with the temperature required to achieve 99% destruction by thermal oxidation, as reported by Taylor and Dellinger.²⁰ The EPA²¹ has ranked these compounds from the most difficult to the least difficult to incinerate thermally as: CCl₄, CH₂Cl, CH₂Cl₂, CH₃Cl.

The slightly easier destruction of some fluorinated hydrocarbons relative to their chlorinated analogues (over the new HDC) is illustrated in Figure 12; the temperatures required for 99% conversion are 280°C and 320°C for fluorobenzene and chlorobenzene, respectively at these conditions. Similarly, 1,2-difluoroethane and 1,2-dichloroethane were found to give very similar conversion-temperature curves over the HDC, as illustrated for the former in Figure 13. That figure also shows the greater ease of catalytic destruction of the geminal dihaloethanes (1,1-difluoroethane) relative to the vicinal compound (1,2-difluoroethane). This difference is also consistent with a greater ease of destruction by the HDC of the compound with a weaker halocarbon bond as was found for the series of chloromethanes (Figure 11).

<table>
<thead>
<tr>
<th>LBDE</th>
<th>T-99%, Thermal</th>
<th>T-99%, HDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ch₂Cl</td>
<td>83.5</td>
<td>805°C</td>
</tr>
<tr>
<td>CH₂Cl</td>
<td>79.0</td>
<td>755</td>
</tr>
<tr>
<td>CHCl</td>
<td>77.0</td>
<td>595</td>
</tr>
<tr>
<td>CCl₄</td>
<td>70.4</td>
<td>750</td>
</tr>
</tbody>
</table>

It is clear that the relative ease of breaking the weakest chlorocarbon bond correlates well with the relative ease of destruction by the HDC, and is probably the factor which determines the relative ease of destruction. This is, of course, obviously not the determining factor in their destruction over the Pt-Al₂O₃ catalyst of Bond and Sadeghi.²³
Figure 11. Destruction of the C-1 chlorocarbons over HDC: 1.5% H₂O in air at 15,000 hr⁻¹ GHSV (STP). Chlorocarbon concentrations: CCl₄-900 ppmv; CHCl₃-500 ppmv; CH₂Cl₂-800 ppmv; CH₃Cl-600 ppmv.
Figure 12. Destruction of chlorobenzene and fluorobenzene over monolithic HDC: 9.5% H₂O, 12% O₂, at 15,000 hr⁻¹ GHSV (STP), 100 ppmv of C₆H₅Cl or C₆H₅F.

Figure 13. Destruction of 1,1-difluoroethane and of 1,2-difluoroethane over monolithic HDC: 1.5% H₂O in air at 15,000 hr⁻¹ GHSV (STP), 400 ppmv of C₂H₄F₂.
CONCLUSION

Results have been presented for the destruction of a number of diverse chlorinated and fluorinated hydrocarbons over a monolithic or particulate form of a new proprietary catalyst, referred to as a halohydrocarbon destruction catalyst (HDC). The HDC appears to be significantly more active, stable, and insensitive to inhibition by halogen, than the supported noble metal or chromia-alumina catalysts previously described. The relative ease of destruction of a particular series of halohydrocarbon over the new Allied-Signal halohydrocarbon destruction catalyst appears to be determined by the bond dissociation energy of the weakest halocarbon bonds in the halohydrocarbon, rather than being inversely proportioned to the number of halogen atoms per molecule.
REFERENCES


15. W. K. Hunter, L. C. Hardison and E. J. Dowd, (to Air Resources Inc.), U.S.
Patent 4,330,513 (May 18th, 1982).

16. M. A. Pallazolo, C. L. Jamgochian, J. I. Steinmetz and D. L. Lewis, "Destruction of

17. R. A. Ashworth, M. A. Pallazolo and B. A. Tichenor, "Destruction of organic contaminants


20. P. H. Taylor and B. Dellinger, "Thermal degradation characteristics of chloromethane

21. USEPA; "Presentation of method for the selection of POHC's in accordance with the RCRA
interim final rule, incineration standards," January 23, 1981, Office of Solid Waste,
August 31, 1981.

22. D. L. Miller, D. W. Senser, V. A. Cundy and R. A. Matula, "Chemical considerations in the