

Catalytic Removal and Oxidation of Chlorinated Hydrocarbons

B. Kline and J. Tavakoli¹

The oxidation reactions of trichloroethylene (TCE) and 1,2,4 trichlorobenzene (TCB) on sodium carbonate supported catalyst were studied to identify the reagent loss. Four different batches of catalysts provided by Berty Reaction Engineers, Ltd. (BREL) were examined in this project. All four catalysts effectively destroyed TCE and TCB (> 99.99%) at temperatures below or about 550°C. The catalysts used in this study were all magnesium/manganese base catalysts.

INTRODUCTION

The Clean Air Act Amendments of 1990 (CAAA) require stringent limitations on emission of about 200 air pollutants by the chemical industry. All major sources of volatile organic chemicals (VOCs) located in ozone non-attainment zones (almost all major metropolitan areas) will be required to install reasonably available control technology (RACT). RACT is defined as the lowest emission limit that a particular source can meet by the application of control technology that is reasonably available considering technological and economical feasibility.

Volatile organic chemical and halogenated hydrocarbons (HHCs) are manufactured and used on a large scale in a significant number of chemical industries. Incineration is the most suitable technology for ultimate destruction of these chemicals. However, high temperature oxygen-rich incineration often seems to produce trace amounts of undesirable and thermally stable combustion products. In addition, a

major product of high temperature halocarbon oxidation is halogenated acid (HCl, HBr, etc.). The free acid is highly corrosive in a moistured oxidizing environment, requiring expensive materials of construction and an effective acid removal step. Moreover, the process is costly and problematic in handling waste streams with low heating value; that is, streams with a high concentration of chlorocarbons [1-3]. In treating chlorocarbons, for example, even if the parent compound is completely destroyed in the incinerator, the reaction products may not all be carbon dioxide, water and hydrochloric acid. In a fuel lean combustion atmosphere the formation of more thermodynamically stable H₂O obstructs the production of HCl and favors the generation of unwanted compounds (Cl₂, Cl_xO_y) and/or the persistence of carbon-chlorine bonds. It has been shown that the pyrolysis of chlorocarbons, on the other hand, is a strongly sooting process [4-6].

Catalytic incineration is another treatment technology considered for ultimate disposal of VOCs and HHCs. A thorough re-

1. Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA.

view of catalytic decomposition of halogenated hydrocarbons has been published by Spivey and Butt [7]. Kosusko and Nunez [8] have reported that above 95% HHCs removal efficiency can be achieved over metal oxide catalysts at a temperature range of 1,000-1,200 F. A copper and manganese oxide catalyst was positively tested on the destruction of a variety of air pollutants, including HHCs [9]. While effective in destruction of HHCs, all these catalysts release HCl, Cl₂, H₂O and CO₂. This acidic product stream requires similar after burner treatments as the thermal processes for acid removal and demands a corrosion resistant reactor. Similar results have been reported on catalytic hydrodechlorination and dechlorination of chlorinated hydrocarbons [10-15].

In this paper, we report the results of a study on decomposition of TCE and 1,2,4 TCB on a catalyst developed and patented by Berty Reaction Engineers, Ltd. [16]. This process uses catalytically activated sodium carbonate to remove and destroy HAZs efficiently and at a minimum cost. It has shown to effectively destroy a wide range of VOCs and HHCs considered as hazardous air pollutants (HAZ) by the CAAA [17]. The catalytic metals and support materials are environmentally friendly and the spent catalyst is easy to regenerate or dispose of. Typical support materials include limestone, magnesium, manganese or copper oxide, and sodium carbonate. This carbonate-

based catalyst combines the oxidation and acid removal steps mentioned above. In this process, the acid formation is circumvented by the direct reaction of chlorine with the catalyst metal followed by the catalytic chloride (CuCl₂, MgCl₂) reaction with the support, Na₂CO₃. That is, the organic halogen reacts with the support and produces a nontoxic alkali or alkaline-earth salt as opposed to other processes in which dissociated halogen results in HCl, Cl₂, HBr, etc.

EXPERIMENTAL

Apparatus

The performance of several alkali carbonate supported catalysts were examined in two tubular flow reactors connected in series. The schematic diagram of the experimental apparatus is shown in Figure 1. Both reactors, 1/2 in S.S. tubing approximately 15 in long each, were housed in a vertical clam-shell furnace. The two reactors were interconnected by a three-way valve, permitting the effluent of the first reactor to be bypassed by the second reactor and directed to an on-line gas chromatograph (GC) for analysis. The furnace temperature was kept constant during each run using an Omega 920 temperature controller. J-type thermocouples and indicators (Omega) were used to read the temperatures in the reactors and the furnace. The furnace temperature could reach as high as 650° C.

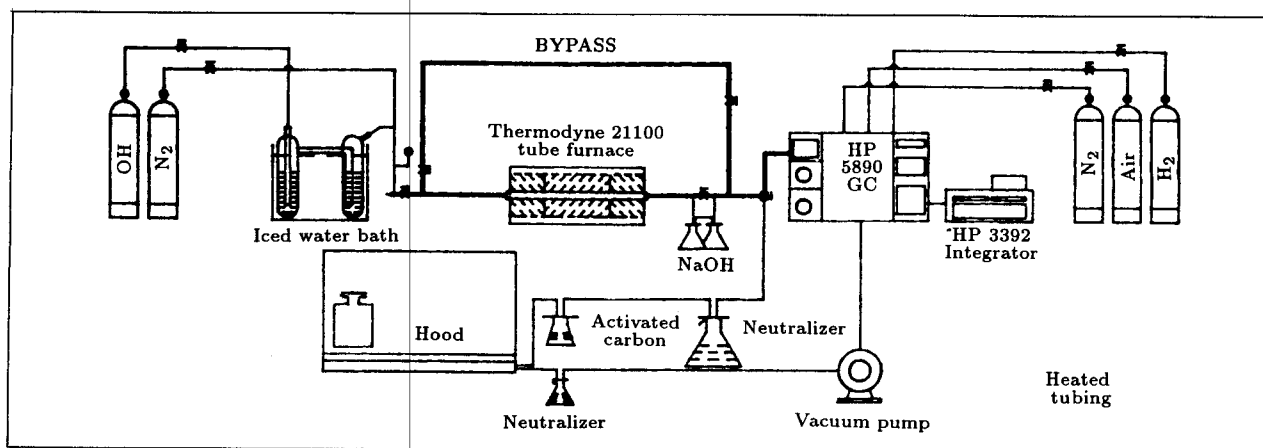


Figure 1. Experimental apparatus.

Materials

TCE and TCB (> 99%) were obtained from Aldrich. Four different batches of catalysts were provided by Berty Reaction Engineers, Ltd. which were numbered as received. Zero grade air cylinders were from Wilson Products.

Operating Procedure

Two zero grade air streams flowing in parallel are mixed before entering the reactor. One of the streams is passed through a bubbler (1/2 in S.S. U-tube filled with glass beads) containing TCE or TCB and the second one is moisturized in a stainless steel cylinder filled with water. Each reactor was charged with approximately three grams of catalyst with known volume. The flow rate of both air streams was held constant throughout each run. The gas hourly space velocity (GHSV) used in these experiments ranged from 5,000 to 11,000 for each reactor. "Lightoff" curve was produced for each catalyst by increasing the reactor temperature from 25°C to 550°C or more when needed. The longest time that the reactors were operated continuously was 16 hours.

Analysis

An on-line Hewlett Packard 5890 gas chromatograph (GC) equipped with FID was used for the analysis of each reactor effluent or the bypass stream. Three different packed columns were used to separate the species in product stream, SP1100 for TCE, and SP2250 for TCB. A small fraction of the reactor effluent was directed to a constant volume (1 ml) sampling loop installed on 6-port Valco valve. The valve was operated by an actuator connected to a 70 psig nitrogen line. The rest of the product stream was passed through a flask containing 75 ml 0.014 N silver nitrate, for HCl analysis, before purging into the hood.

RESULT AND DISCUSSION

TCE

TCE was tested at a feed concentration of 57 ppmv and GHSV of 10800 on catalyst No. 3. The lightoff curve for TCE is shown in Figure 2.

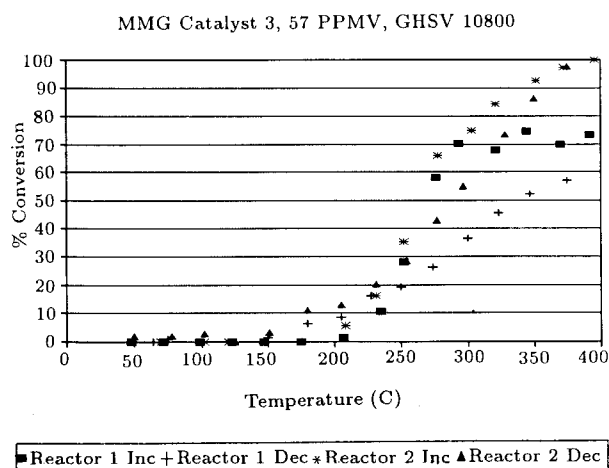


Figure 2. Lightoff curve for TCE.

At this GHSV, the complete destruction of TCE occurred at 396°C. Figure 2 indicates that T50 occurs at 260°C and T90 at 340°C for this space velocity. Decay of TCE as a function of temperature is illustrated in Figure 3.

This figure indicates that more than 70% of the contaminant (TCE) is treated in the first reactor and reactor two decomposes the remaining portion. Figure 4 illustrates the change in concentration of the contaminant with time and temperature. At GHSV of 10800 and 57 ppmv of TCE, catalyst No. 3 started destroying the contaminant at about 200°C. A significant difference was noticed between T50 (temperature at which 50% of the contaminant was destroyed) and T90 of catalysts No. 2 and No. 3. Catalyst No. 2 completely

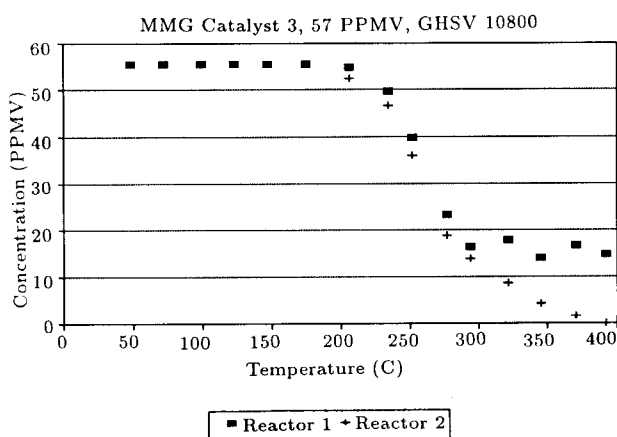


Figure 3. Decay of TCE vs. temperature.

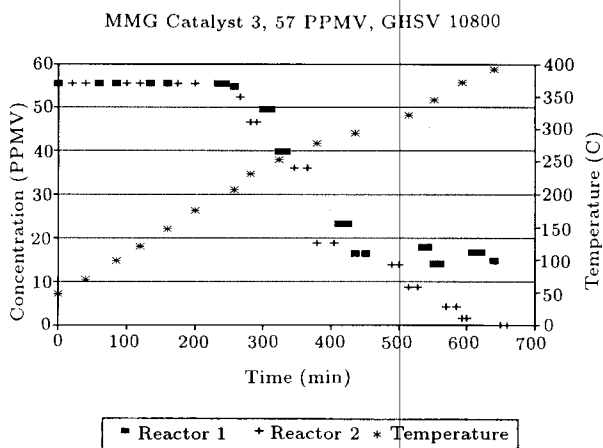
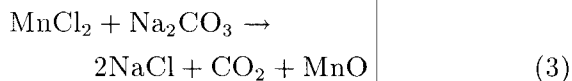
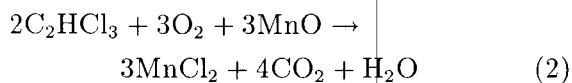
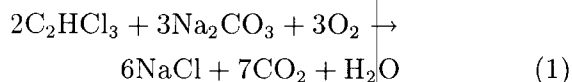


Figure 4. Decay of TCE vs. time.

destroyed TCE at 276°C as opposed to 396°C over catalyst No. 3. Since the chemistry of the two catalysts were believed to be the same, the difference in GHSV used should have contributed to the temperature difference for ultimate destruction of trichloroethylene. In the first case (catalyst No. 2) the GHSV was 6850 and in the second (catalyst No. 3) 10800.

While a detailed kinetic analysis is ongoing, the overall catalytic reactions for the destruction of TCE are suggested to involve a gas/solid/solid reaction [17]. The first step is a gas/solid oxidation reaction which destroys TCE and converts the metal oxides of the catalyst (MnO/MgO) to metal chlorides. The second step is a phase reaction between the metal chlorides and the support matrix (Na₂CO₃). The second step is a solid/solid phase reaction between the metal chloride and the support matrix. This reaction regenerates the metal oxide and forms the stable salt NaCl from the sodium carbonate support. The reactions of TCE that occur on the catalyst surface can be summarized as follows:



This reaction is thermodynamically favored at

low temperatures. The free energies for Reactions 2 and 3 at 300°C are -498 Kcal/mol and -9 Kcal/mol respectively.

TCB

Figures 5 and 6 present the results obtained on the decomposition of 1,2,4 TCB over catalyst No. 4. The gas hourly space velocity throughout the experiment was kept constant at 7550 and the TCB concentration level of the main stream entering the reactor was 31 ppmv. While destruction of the parent compound starts at about 200°C, it is not completed before the reactor temperature reaches 557°C. At this point, more than 90% of the TCB in the entering stream is converted in the first reactor and the second reactor was required to eliminate the rest of it. The presence of other species was noticed in the effluent of

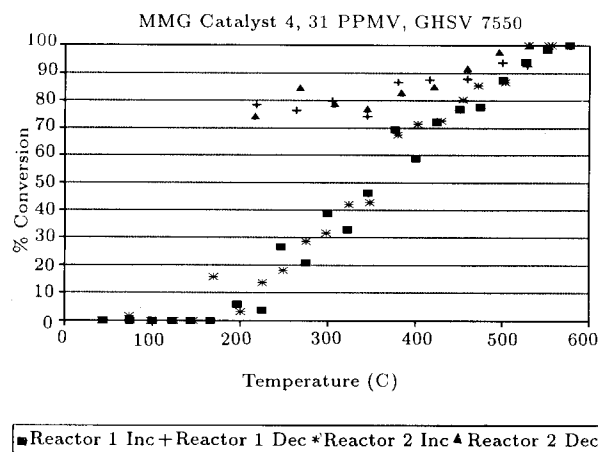


Figure 5. Lightoff curves for TCB.

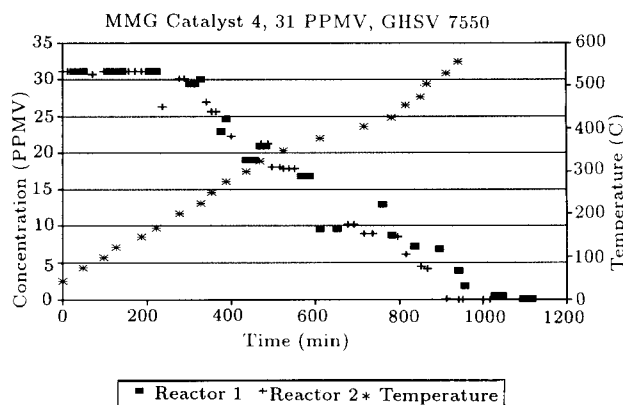


Figure 6. Decay of TCB vs. time.

the reactor indicated by peaks other than that of TCB on the chromatogram. At 557° C, no other species were identified in measurable quantities by the FID detector. Figure 6 shows the decay of TCB with time and temperature. This figure indicates that T50 and T90 of TCB over catalyst No. 4 at GHSV of 7550 occurred at 350° C and 510° C, respectively.

CONCLUSION

We have shown that the activated sodium carbonate catalyst effectively destroyed TCE and 1,2,4 TCB at temperatures 396° C and 557° C in two flow reactor systems connected in series. Gas hourly space velocities ranging from 5,000 to 11,000 were used for each reactor. While most of the contaminants (more than 70%) were destroyed in the first reactor at all temperatures and GHSVs, the second reactor was necessary for the complete destruction of contaminants.

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REFERENCES

1. Graham, J.I., Hall, L.H. and Dellinger, B. "Laboratory investigation of thermal degradation of a mixture of hazardous organic compounds", *Environ. Sci. Technol.*, **20**, p 703 (1986).
2. Oberg, T., Aittola, J.P. and Bergstrom, J.G.T. "Chlorinated aromatics from the combustion of hazardous waste", *Chemosphere*, **14** (2), p 215 (1985).
3. Taylor, P.H. and Dellinger, B. "Thermal degradation characteristics of chloromethane mixtures", *Environ. Sci. Technol.*, **22**, p 438 (1988).
4. Garner, F.H., Long, T., Graham, A.J. and Badakhshan, A. "The effect of certain halogenated methanes on pre-mixed and diffusion flames", Sixth Symposium (international) on Combustion, Reinhold, New York, USA, p 108 (1957).
5. Robinson, J.M., Gupta, A.K. and Senkan, S.M. "Sooting limits of chlorinated hydrocarbon-methane-air premixed flames", *Combust & Flame*, **49**, p 305 (1983).
6. Frenklach, M., Hsu, J.P., Miller, D.L. and Matula, R.A. "Shock-tube pyrolysis of chlorinated hydrocarbons: formation of soot", *Combust & Flame*, **64**, p 141 (1986).
7. Spivey, J.J. and Butt, J.B. "Literature review: deactivation of catalysts in the oxidation of volatile organic compounds", *Catalysis Today*, **11**, p 465 (1992).
8. Kosusko, M. and Nunez, C.M. "Destruction of volatile organic compounds using catalytic oxidation", *J. Air Waste Manage. Assoc.*, **40** (2), p 254 (1990).
9. Musick, J.K. and Williams, F.W. "Catalytic decomposition of halogenated hydrocarbons over hopcalite catalyst", *Ind. Eng. Chem. Res.*, **13** (3), p 175 (1974).
10. Weiss, A.H., Valinski, S. and Antoshin, G.V. "Hydrodechlorination and oligomerization of carbon tetrachloride over nickel Y zeolites", *J. Catal.*, **74**, p 136 (1982).
11. LaPierre, R.B., Wu, D., Kranich, W.L. and Weiss, A.H. "Hydrodechlorination of 1, 1-bis(p-chlorophenyl)-2, 2-dichloroethylene (p,p'-DDE) in the vapor phase", *J. Catal.*, **52**, p 59 (1978).
12. Van Barneveld, W.A.A. and Ponec, V. "Reactions of $\text{CH}_x\text{Cl}_{4-x}$ with hydrogen: relation to the Fischer-Tropsch synthesis of hydrocarbons", *J. Catal.*, **88**, p 382 (1984).
13. Coq, B., Ferrat, G. and Figuera, F.J. "Conversion of chlorobenzene over palladium and rhodium catalysts of widely varying dispersion", *J. Catal.*, **101**, p 434 (1986).

14. Fung, S.C. and Sinfelt, J.H., "Hydrogenolysis of methyl chloride on metals", *J. Catal.*, **103**, p 220 (1987).
15. Chuang, S.C., Bozzelli, J.W. and Chen, Y.M. "Catalytic hydrodechlorination of 1,2-dichloroethane and trichloroethylene over Rh/SiO₂", *Chem. Eng. Comm.*, **115**, p 1 (1992).
16. Berty, J.M. United States Patent 5,021,383, June 4, 1991, to Berty Reaction Engineers, Ltd., Fogelsville, PA, USA.
17. Stenger, H.G., Buzan G.E. and Berty, J.M. "Chlorine capture by catalyst-sorbents for the oxidation of air pollutants", AIChE Annual Meeting (Nov. 1992).