

Development of transition metal oxide-zeolite catalysts to control chlorinated VOC air emissions

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Transition metal oxide (TMO)-zeolite oxidation catalysts have been developed to control chlorinated volatile organic compound (CVOC) emissions. Research has been initiated to enhance the utility of these catalysts by the development of a sorption-catalyst system. Zeolites with a high Al/Si ratio (e.g., Y-zeolite) provide active acid exchange sites. The exchanged and calcined zeolite is impregnated with the same or different metal and calcined to form the TMO film. These TMO-zeolites provide shape selectivity and three types of active sites: unexchanged HY (Brönsted) acid active sites, highly active exchanged sites, and impregnated TMO sites. They can achieve over 95% destruction efficiency at relatively low temperatures (i.e., 300 to 350°C) of a humid, low concentration CVOC, and are very resistive to poisoning. In the sorption-catalyst system, the zeolite first would physically adsorb the CVOC at room temperature. The system would then be heated to promote the TMO-zeolite catalytic reaction. The Y-zeolites can physically adsorb about 5% VOC but are highly hydrophilic. Silicalite is a zeolite with very little Al, can adsorb up to 15% VOC, and is hydrophobic. Impregnated Silicalite is an effective adsorbent and fair catalyst.

1. INTRODUCTION

CVOCs from both air streams and remediation of contaminated waste waters can be destroyed economically through catalytic incineration. The catalytic incineration of humid, dilute CVOCs from stripping contaminated waste waters is cheaper and more effective than carbon adsorption (either of water or stripping air) [1]. While noble metals can very effectively destroy VOCs, they are very easily poisoned by the products (specifically HCl) and by-products (specifically Cl₂) of oxidizing CVOCs [2].

TMO-zeolite catalysts can destroy dilute or concentrated CVOC streams, which are wet or dry, at relatively low temperatures without the formation of dangerous by-products, such as dioxins. In the 300 to 350°C range with a space velocity of 3000 h⁻¹, the reaction is first order with respect to the CVOC and over 95% efficient.

Experimental work has focused upon the following CVOCs: methylene chloride (MeCl₂), carbon tetrachloride (CCl₄), and trichloroethylene (TCE). Cobalt exchanged zeolites (Co-Y) are very effective in destroying single carbon CVOCs. However, the use of chromium, either in the exchanged or impregnated form, appears needed to destroy double bonded CVOCs. The TMO-zeolite catalysts strongly promote the deep oxidation of the chlorine atoms in the CVOC to HCl with no other chloride by-product other than Cl₂ being detected. However, CO rather than CO₂ often is favored.

2. EXPERIMENTAL

2.1 Materials

The zeolites tested were H-Y, a faujasite-type zeolite with a three dimensional structure and high $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio; and Silicalite, a zeolite with essentially no Al_2O_3 . The H-Y was 1/16-inch (1.6 mm) LZ-Y64 pellets obtained from Union Carbide. The Silicalite was made into pellets by bonding its powder with Silbond and then impregnated.

The catalysts tested were zeolites exchanged or impregnated with first row transition metals (TM). In our nomenclature, TM-zeolite represents an exchanged TMO-zeolite. A slash (/) following the zeolite shows the impregnated TM cation and its salt or acid that was used to impregnate the zeolite. For example, Co-Y/CA is a cobalt exchanged Y-zeolite which was impregnated with chromium using chromic acid.

2.2 Apparatus

The experimental setup is shown elsewhere [3]. A 25 mm I.D., 1 m long Pyrex tube normally was packed with 5.4 cm of catalyst. For 500 cm^3/min reactant flow, a space time of 3000 hr^{-1} would result. The reaction temperature was controlled within 1°C of the 250 to 400°C setpoint by the two Lindberg tubular furnaces surrounding the Pyrex tube. Sorbent breakthrough data were obtained with sorbent challenged by reactant run at room temperature. Breakthrough was reported when the outlet concentration exceeded 5% of the inlet concentration.

2.3 Analysis

Reactant feed and product samples were collected with Hamilton CR 700-200 constant rate syringes. These samples were injected for analysis into an HP 5890 GC followed by an HP 5970B mass selective detector (GC/MS). Oxygen and CVOC pickup were determined at 300°C with a thermogravimetric analyzer (TGA). This TGA consists of a DuPont Model 2100 thermal analysis system with a 2950 TGA.

Surface areas were determined with a Quantachrome Quantasorb Jr. BET surface area analyzer. Catalyst and sorbent compositions were determined using a Philips PV9550 energy dispersive X-ray fluorescence (XRF) spectrometer. Zeolite acidities were obtained using the TGA by temperature programmed desorption (TPD) of ammonia previously adsorbed at 100°C .

All experimental measurements were made in accordance with EPA Air and Energy Engineering Research Laboratory Quality Assurance Category 3 criteria. For example, three to five CVOC GC/MS samples were taken for each run at inlet and outlet, and the outlet concentration is accurate to ± 10 ppmv.

2.4 Procedures

The procedures for preparing Co-Y/CA are described elsewhere [3]. The Silicalite/CA powder was bonded with Silbond for pellet formation and then impregnated. Additional information on preparing these pellets and powders washcoated onto a low-surface-area inert cordierite core for support is provided in Reference 4.

3. RESULTS

3.1 Catalyst Characteristics

Table 1 gives BET, XRF, and acidity results for selected catalysts whose conversions and selectivity are reported. The typical H-Y, from which most of the above catalysts were made, had a surface area of $550 \text{ m}^2/\text{g}$, a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1.6, and $0.05 \text{ g NH}_3/\text{g}$ [3]. Thus properly prepared, cation addition does not significantly reduce surface area or $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, and appears to slightly decrease the acidity.

3.2 Conversion

Figures 1 and 2 show the conversion of MeCl_2 with one CCl_4 run and of TCE, respectively. As expected, conversion falls for decreasing temperature. These figures show that the use of Co in these catalysts is very effective in destroying MeCl_2 (see Figure 1) but not suitable for destroying TCE (see Figure 2).

Table 1
Catalyst Characteristics and Run IDs

Catalyst ^a	Surface Area (m ² /g)	SiO ₂ / Al ₂ O ₃	Catalyst Cation(%)	Acidity (g NH ₃ /g)	Run TCE	ID ^b MeCl ₂
Cr-Y	440	1.58	2.17	0.042	1-4	5-8
Co-Y/Co	524	1.56	4.6	0.039	--	9-11
Co-Y/CN	419	1.61	3.34/5.95		12-14	15-16
Sil/CA	370	high	10.98	0.005	17-20	--
Mixed bed ^c					26-29	21-22 ^d
Co-Y/CA	330	1.77	1.96/5.47	0.0	30-33	--
Co-Y/CR	521	1.56	3.47/4.95	0.045	34-37	--
Cr-Y/Co	388	1.59	1.71/5.47	0.048	38-40	--
Co-Y	560	1.56	1.1	0.046	41-43	--

a All runs at approx. 2400 h⁻¹ and 13,000 ppm added water.

b See Figures 1 and 2, respectively, for MeCl_2 and TCE runs. Note all runs are in descending temperature order.

c Mixed bed is a physical mixture 50% each by weight Cr-Y and Silicalite/CA.

d Runs 23, 24, and 25 were CCl_4 whose conversion is in Figure 1.

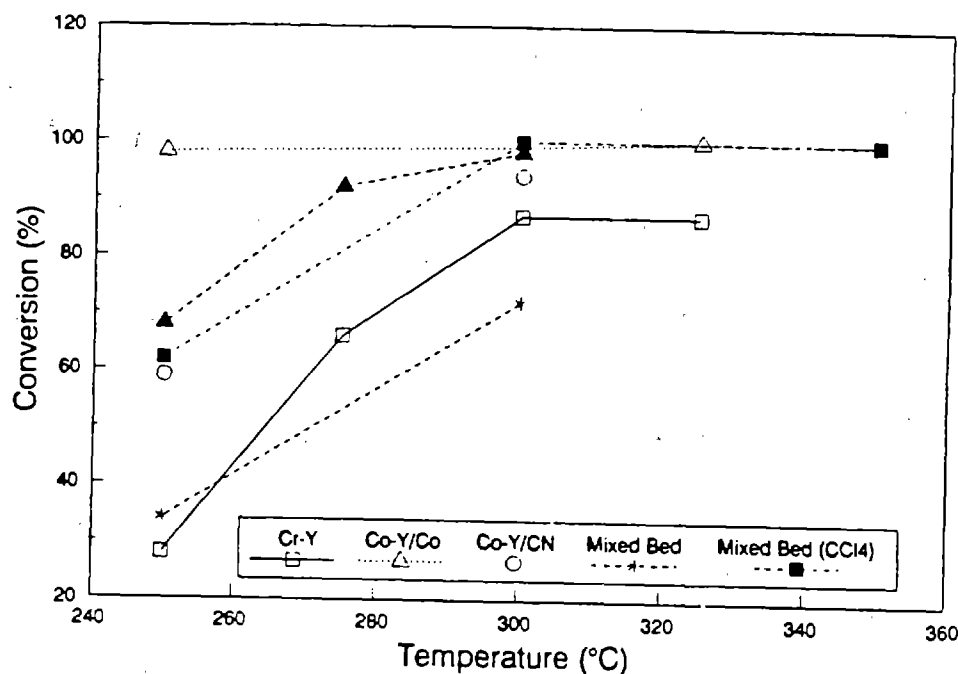


Figure 1. Conversion of single carbon CVOCs

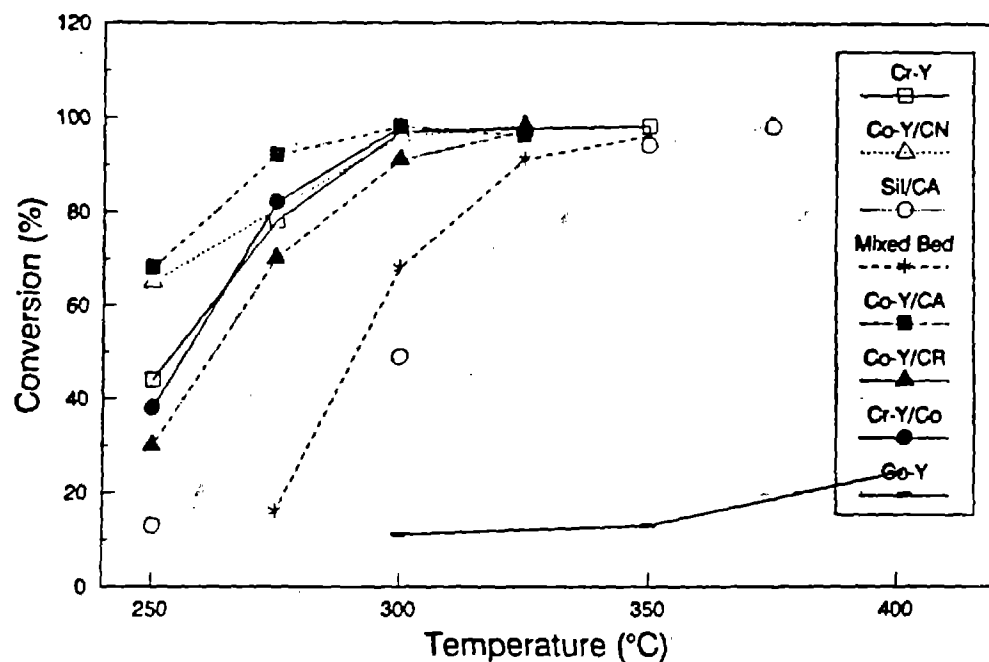


Figure 2. TCE conversion

The extent to which the mass balances for carbon and chlorine are closed (closure %) is shown in Figure 3. For the 43 runs selected, closure % for carbon averaged 90.2% and closure % for chlorine averaged 98.8% with standard deviations of 12.5 and 12.1, respectively. These closure %'s are calculated based on the measured inlet CVOC and CO₂ and outlet product concentrations.

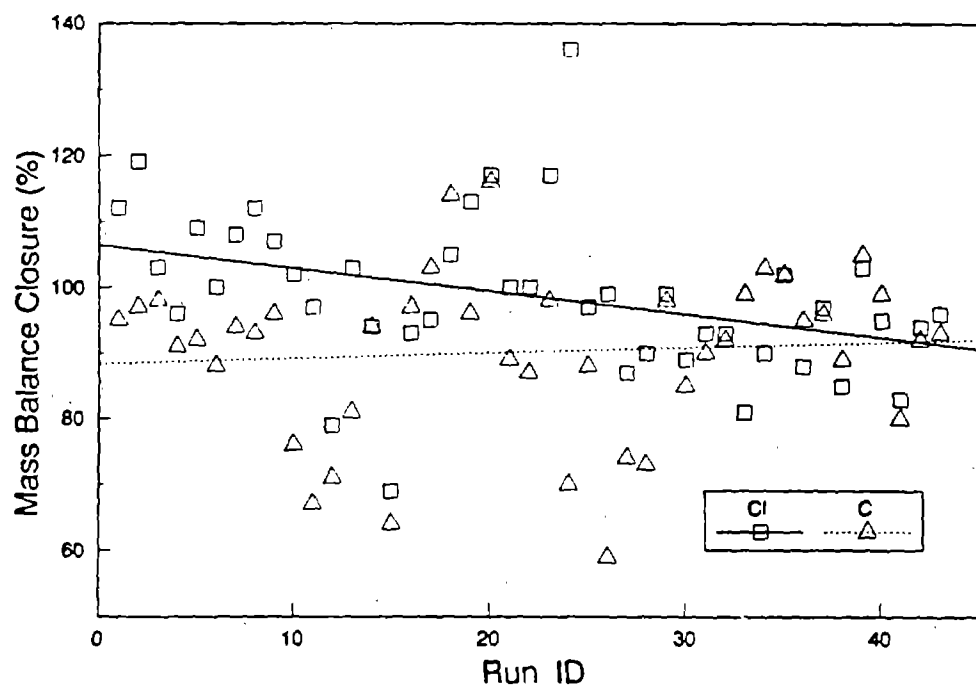


Figure 3. % Closure on Mass Balances for Carbon and Chlorine

3.3 Selectivity

Note that all the above runs were made with addition of about 13,000 ppm of water vapor. Figure 4 gives the production ratios for the CO/CO₂ and Cl₂/HCl. Use of the Run IDs as defined in Table 1 will give the catalysts/CVOC combinations, and the temperatures are in Figures 1 and 2 for single carbon CVOCs and TCE, respectively. For example, run ID 30 which has the highest Cl₂ production is a TCE run at 325 °C using Co-Y/CA (see Figure 2). The Cl₂/HCl ratios for TCE are much higher than those for MeCl₂. However, this Cl₂ production varies for different catalysts. For example, CrY produces significant Cl₂ during TCE oxidation [runs 1-4] while CoY/CN [runs 12-14] shows no detectable Cl₂ formation. Similarly, CO production with TCE is about five times greater with CrY than with SiI/CA catalyst. Only CO₂ is formed in the oxidation of a humid CCl₄ stream with a total absence of CO as exemplified by run IDs 23, 24, and 25.

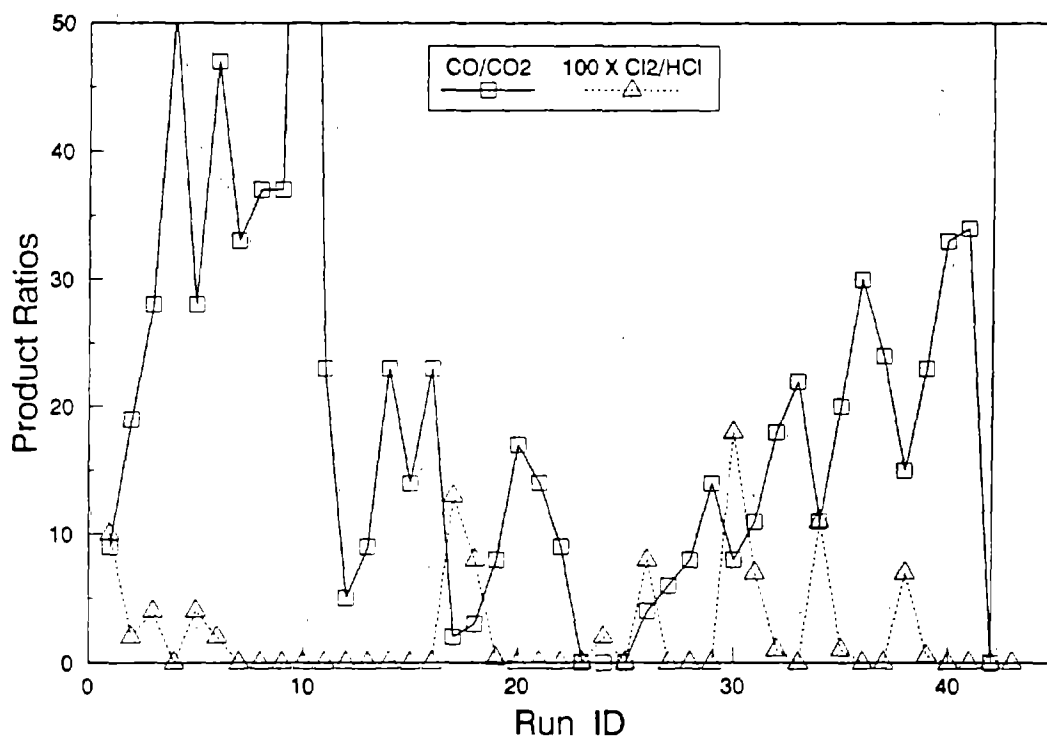


Figure 4. Chlorine and carbon products

3.4 Deactivation

Table 2 shows some selected deactivation results. During these tests, the catalyst was continuously challenged for 12 days with wet (approx. 13,000 ppm water) CVOC feed at 600°C except for short periods when the temperature was reduced to 275°C to measure conversion. The catalyst cation and surface areas dropped only slightly. However, significant losses in conversion, oxygen and TCE pickup, and acidity were observed. Figure 5 shows the falloff for several of these catalysts at various times during these deactivation studies. For these TMO-zeolite catalysts, the chromium exchanged catalysts appear much more stable than the chromium impregnated ones.

Table 2
Characteristics of Fresh and Aged Catalysts

Catalyst	Age (days)	Surface Area (m ² /g)	SiO ₂ /Al ₂ O ₃	Catalyst Cation (oxides)(%)	Oxygen Pickup (%)	TCE Pick-up(%)	Conv. (%)	Acidity (g NH ₃ /g)
Cr-Y	0	440	1.58	2.17	3.53	3.31	92	0.042
	12	412	1.59	1.54	1.53	1.39	75	0.031
Co-Y/CN	0	419	1.61	3.34/5.95	3.30	2.75	92	0.041
	12	339	1.46	3.22/5.37	2.33	0.96	43	0.032
SiI/CA	0	370	high	10.98	--	--	72	0.005
	12	331	--	9.98	--	--	33	--
Co-Y/CA	0	330	1.77	1.96/5.47	3.20	1.73	95	0.043
	12	250	1.73	1.92/5.03	1.87	1.18	50	0.034
Co-Y/CR	0	521	1.56	3.47/4.95	3.61	3.75	90	0.045
	12	440	1.56	3.32/3.84	1.76	1.12	33	0.037
Cr-Y/Co	0	388	1.59	5.47/1.71	3.51	4.30	90	0.048
	12	348	1.57	5.40/1.48	2.60	0.91	76	0.036

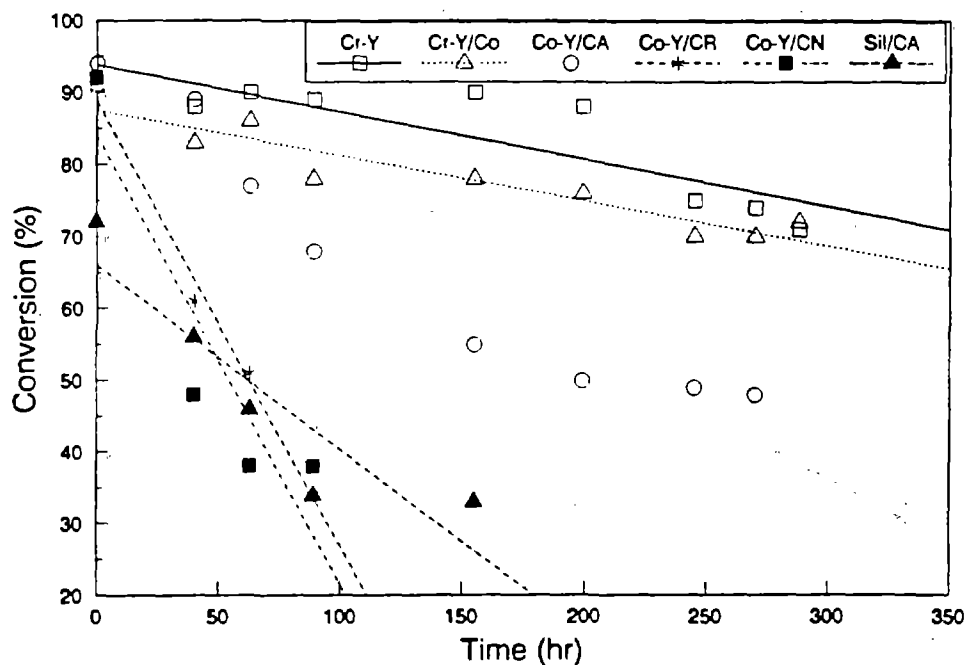


Figure 5. Catalyst deactivation with time

3.5 Sorbents

Table 3 shows the capacity and breakthrough data for some of the sorbents tested to date. As expected, the zeolites tested to date do not have as high an adsorption capacity as carbon for the CVOCs. However, the zeolites do not lose their capacity as rapidly at lower CVOC concentrations and do not appear to be adversely affected by relatively high levels of water vapor.

Table 3
Collected Sorption Results

ID ^a	Catalyst	Adsorbate	Adsorb Conc (ppmv)	Water Conc (ppmv)	Break-through Capacity ^b	Saturation Capacity ^b
1	Carbon	TCE	1181	12,114	36.0	40.0
2	Carbon	TCE	240	13,918	20.0	27.0
3	Carbon	MeCl ₂	250	14,265	3.6	5.0
4	Silicalite	TCE	1050	14,632	10.6	16.9
5	Cr-Y	TCE	1125	none	2.2	5.9
6	Sil/CA	TCE	1049	11,115	8.6	14.7
7	Mixed Bed ^c	TCE	1100	10,902	5.8	10.4
8	Mixed Bed	TCE	240	14,000	6.1	9.4
9	Mixed Bed	MeCl ₂	1050	12,151	3.3	5.5
10	Mixed Bed	CCl ₄	1055	12,051	2.0	3.8

^aAll runs were carried out at 23°C and at a space velocity of 2360 hr⁻¹.

^bReported capacities are weight percent adsorbate adsorbed per adsorbent.

^cMixed bed consisted of a 50-50 weight percent (wt %) physical mixture of Silicalite/CA and Cr-Y.

4. DISCUSSION

4.1 Activity

Properly prepared TMO-Y catalysts using several of the first row transition metals give excellent activity in the oxidative destruction of single carbon HVOCs. However, no data gave satisfactory TCE destruction using TMO-Y catalysts without the use of chromium. The modified Co-Y catalysts used in Reference 5 were modified to Co-Y/CA catalysts by impregnating them with chromic acid. Much data exist (e.g., Figures 2 and 3 and Reference 5) that show greater than 95% CVOC destruction in the 300 to 350°C temperature range and space velocities of about 3000 hr⁻¹. Reference 6 shows the expected falloff of conversion with increasing space velocity. Temperatures of less than 275°C, with initially satisfactory conversion, are often unsatisfactory due to activity loss caused by coking [5].

However, the acidity data in Table 1 are largely incomplete. The strength of acid sites is better reflected by the peak ammonium desorption temperature [3]. This peak temperature acidity is more indicative of catalyst activity than is total ammonium adsorption/desorption.

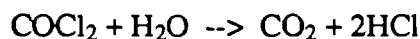
4.2 Mechanisms and Selectivity

The CO/CO₂ ratios do not appear to be affected by the addition of water. However, the introduction of water can have a significant effect on Cl₂ production. For example, at 300°C the percent Cl₂ increased from the 0 to 2% range with water to about 20% for dry TCE feed [6].

For the TMO-zeolite oxidation of single carbon CVOCs, it is proposed [3] that the HVOC is adsorbed on a Brönsted acid site. It then combines with a proton from this site to form a carbonium ion. Oxygen is adsorbed on a cationic site as a disassociative species (i.e., O) which oxidizes the TM (e.g., from Co⁺² to Co⁺³) and forms O⁻. The carbonium ion reacts with O⁻ to form a surface intermediate and chlorine product.

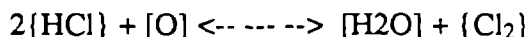
For CCl₄, the surface intermediate is phosgene (COCl₂) or COCl₂H⁺; and the chlorine product is Cl₂. Since HCl is the highly predominant product, this Cl₂ either

remains adsorbed or readsorbs and then desorbs as HCl if sufficient water is present. With a humid feed, COCl_2 reacts with water on the surface or in the vapor phase as:



For MeCl_2 , the surface intermediate is COHCl which decomposes directly to CO and HCl ; and the chlorine product is HCl .

For TCE and Cr-Y, the proposed mechanism [7] will have active cationic sites. Initially, oxygen adsorbs as O^- , as discussed above, followed by the adsorption of an association with TCE at the same site. Then a cyclic intermediary is formed in which the double $\text{Cr}=\text{O}$ and $\text{C}=\text{C}$ bonds are saturated due to the formation of $\text{Cr}-\text{C}$ and $\text{O}-\text{C}$ bonds in this cyclic intermediate. Two paths are proposed: one leads to the formation of two COHCl intermediates and the other to one COHCl and one phosgene. Thus the direct formation of HCl , CO , and some CO_2 is proposed. While some by-product chlorine formation may occur in a parallel reaction, most of the little Cl_2 formed is likely from the Deacon reaction:



(Note: [] and { } represent different sites.)

This reaction appears to be promoted for dry TCE feeds and higher catalyst temperatures. Especially note that the above proposed TCE mechanism sites are Cr cationic rather than the acid sites on which the Cl_2 was adsorbed in the CCl_4 mechanism.

4.3 Sorbent/Catalyst

Y-zeolite has a very high alumina/silicate ratio which provides acid sites, gives it many exchange sites, and makes it an excellent catalyst. However, these same properties make it hydrophilic and a poor adsorbent. Silicalite, a zeolite with very little alumina, has low acidity and very few exchange sites, limiting it to an impregnation catalyst. Cr-Y is a very good catalyst but is a poor adsorbent. Silicalite/CA is a good adsorbent but is only a fair catalyst. The 50-50 wt % mixture of Cr-Y and Silicalite/CA serves both as a good catalyst and good adsorbent. Carbon, an excellent adsorbent, cannot be used because of its inability to withstand the reaction temperature.

Ongoing work includes investigating heat effects on existing catalysts and the use of other zeolites. The 600° C deactivation work, herein reported, suggests that there should be little drop in catalyst activity and likely little drop in physical adsorption capacity due to poisoning or temperature effect. However, possible coking may dictate using temperatures higher than needed for reaction.

4.4 Deactivation and Chromium Issue

The accelerated aging studies were carried out at 600°C, a very severe condition for a high alumina zeolite (Y-zeolite). At these conditions, chromium was lost whether it was exchanged or impregnated, but the exchanged form appears more stable. As previously reported [3], at increased temperature and Cr_2O_3 content, the Deacon reaction increases the Cl_2/HCl ratio for both TCE and MeCl_2 oxidation with the Cr-Y/CA catalyst. Also, Manning [8] found that during the oxidation of perchloroethylene Cl_2 reacted with chromium in the catalyst to form chromium oxychloride (CrO_2Cl_2). However, in our deactivation studies, dark green residue (Cr_2O_3) rather than red-orange (CrO_2Cl_2) was observed. Experimental determinations of these valence states, involving Auger Electron Spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS), would involve a significant change in research approach. Avoiding or explaining possible artifacts, such as might be caused by the high vacuum associated with running XPS, could in itself be a major effort.

Metal sintering also has been observed on metal loaded zeolites. This sintering causes a loss of catalytic surface area due to crystal growth in the catalyst phase. High temperatures promote, and water vapor accelerates this sintering. Two mechanisms [9] for metal crystal growth are (1) crystal migration (movement of metal crystals, collision, and agglomeration); and (2) atomic migration (detachment of metal atoms from crystallites, migration over the surface, and capture by larger crystallites). The loss of BET surface area for both O₂ and TCE as shown in Table 4 reflects the loss of crystallinity and resulting catalyst activity loss.

Several of these deactivation mechanisms suggest that high temperatures, especially at high chromium loadings, promotes much higher Cl₂ levels than would occur otherwise. Current plans are to run long term deactivation studies at a lower temperature (e.g., 450°C).

EPA's current research plan is to find a substitute for chromium in the catalysts used to control TCE and other CVOCs. Efforts to minimize these effects through lower chromium levels that have higher low temperature activity, higher stability, and even higher selectivity (especially those effectively eliminating Cl₂ formation) are underway.

5. CONCLUSIONS

Zeolite catalysts, exchanged or impregnated with transition metal cations, have been specifically compounded to deliver high oxidation activity in destruction of a variety of CVOCs.

By judicious choice of exchanged or impregnated cations zeolite catalyst selectivity may be tailored to produce more CO₂ than CO and to produce HCl with essentially no Cl₂.

Low temperature activity of these catalysts is limited below 275°C by their tendency to reversibly deactivate through a coking process.

Because zeolites can be configured to be both effective catalysts and sorbents, they are potentially useful in a dual role of first physisorbing and then (upon heating) acting as effective catalysts in CVOC control.

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DISCLAIMER

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17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Sorption		Pollution Control	13B
Organic Compounds		Stationary Sources	07C
Volatility Oxidation		Zeolites	20M
Chlorination		Silicalite	07B
Ion Exchange Resins			07D
Catalysis			
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