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6. AUTHOR(S)
Deepak S. Prakash, Kiran V. Athota, Howard L. Greene and Chester A. Vogel

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemical Engineering,
The University of Akron
Akron, OH 44325

Air and Energy Engineering Research
Laboratory, US EPA
Research Triangle Park, NC 27711

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Chlorinated volatile organic compounds (CVOCs) released from water treatment operations (aeration, air stripping, and aerobic biodegradation) are a major source of air pollution. Current technology for recycling or conversion of CVOCs involves carbon absorption followed by stream stripping and destruction using thermal or catalytic means. This process is not only expensive, but also energy and equipment intensive. Considerable economy and efficiency could be affected by utilizing a single dual-function medium capable of catalytically converting them into less harmful products at high temperatures.

The primary aspect of this study was the investigation of zeolite adsorbents, mostly of the ZSM-5 type for their CVOC sorption properties, particularly the sorption of trichloroethylene (TCE), the CVOC of principal interest. Results showed that, due to the competitive adsorption of water, the absorption of TCE decreased significantly. While the presence of presorbed CVOC did not affect subsequent TCE sorption, the dry TCE capacity of chromium-exchanged H-ZSM-5 was considerably reduced with water presaturation of the sorbent. The presence of different exchanged cations in the zeolitic structure did not affect humid TCE sorption levels except with cobalt-exchanged H-ZSM-5 where a significant decrease was noticed.

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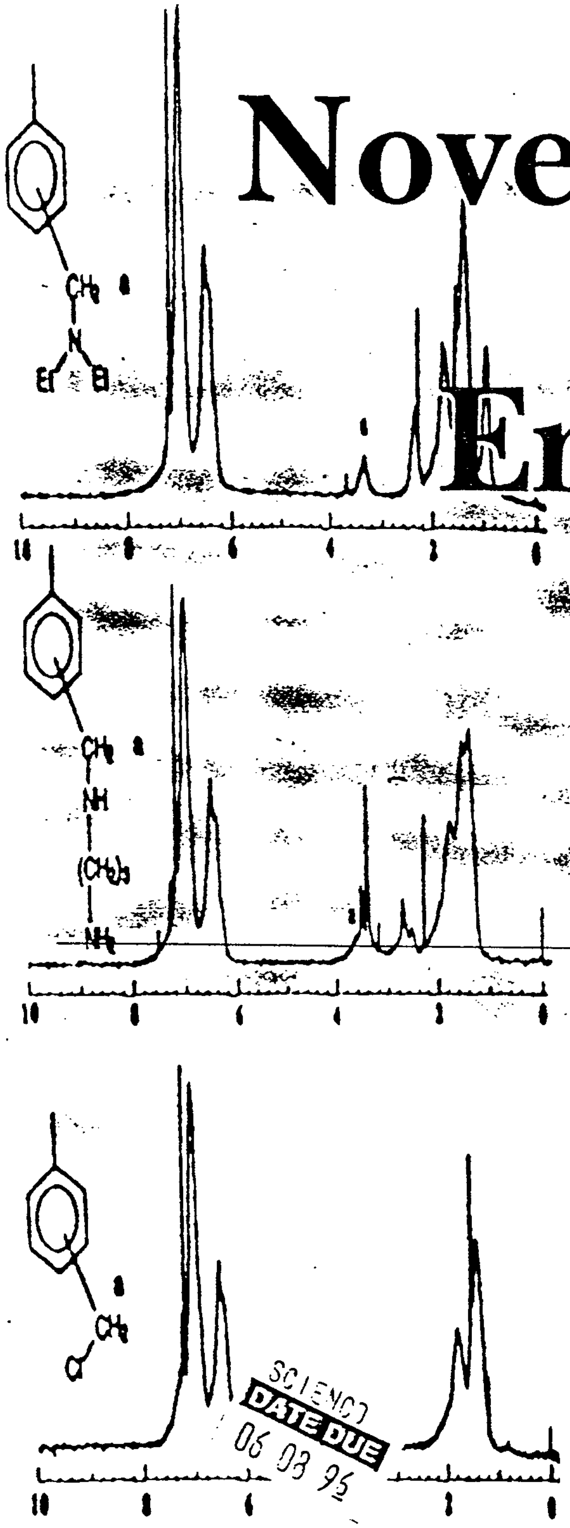

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Sorption and Catalytic Destruction of Chlorinated VOCs Using Fresh and Dealuminated Y and ZSM-5 Zeolites

Deepak S. Prakash, Kiran V. Athota, Howard L. Greene
Department of Chemical Engineering, The University of Akron, Akron, OH 44325

Chester A. Vogel
Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Fresh and dealuminated Y and ZSM-5 type zeolites were investigated for their ability to physically adsorb at ambient temperature and also catalytically destroy chlorinated volatile organic compounds (CVOCs). The sorption of pure component CVOCs [trichloroethylene (TCE), methylene chloride ($MeCl_2$), and carbon tetrachloride (CCl_4)] on chromium-exchanged H-ZSM-5 (Cr-ZSM-5) was studied and Lennard-Jones interactions of these molecules with the ZSM-5 framework were estimated to determine the types of site(s) occupied. The effects of water vapor and presorbed CVOCs on TCE sorption capacities of Cr-ZSM-5 are discussed. While the presence of water vapor either in the feed or as a presorbed compound decreased TCE pickup on Cr-ZSM-5 due to competitive adsorption, presorbed $MeCl_2$ or CCl_4 did not affect subsequent TCE sorption. The presence of chromium or palladium cations in ZSM-5 did not affect humid TCE pickup as compared to hydrogen-exchanged ZSM-5 (H-ZSM-5), but a drop in capacity from 0.079 to 0.04 g TCE/g sorbent was noticed with cobalt-exchanged H-ZSM-5 (Co-ZSM-5). Also in this study, fresh Y and ZSM-5 zeolites were subjected to silicon chloride ($SiCl_4$) dealumination in order to decrease the pickup of water on these zeolites. By changing the number of aluminum atoms per unit cell from 23 to 4 in the Y type, an 80% drop in water pickup was observed; whereas, for the ZSM-5 type, a threefold decrease in the framework aluminum decreased water pickup by approximately75%. Simultaneously, the TCE pickup on the dealuminated zeolites increased significantly as compared to fresh zeolites. Furthermore, the dealuminated Y zeolite showed improved conversion for CCl_4 destruction. Also mentioned in this paper is a process where Cr-ZSM-5 was used as a dual-function medium for first storing and later catalytically destroying a low concentration level (~110 ppm) TCE stream. Considerable energy savings can be obtained by using a single dual-function medium as shown in this paper.

Chlorinated volatile organic compounds (CVOCs) released from water treatment operations (aeration, air stripping, and aerobic biodegradation) are a major source of air pollution [1]. Current technology for recycling or conversion of CVOCs involves carbon adsorption followed by steam stripping and destruction using thermal or catalytic means. This process is not only expensive [2] but also energy and equipment intensive. Considerable economy and efficiency could be effected by utilizing a single dual-function medium capable of adsorbing CVOCs at ambient temperature while also catalytically converting them into less harmful products at high temperatures.

A number of studies [3, 4, 5] have recently investigated the use of transition metal oxide (TMO) catalysts and TMO modified zeolite catalysts for the destruction of dilute CVOCs in humid air. Because of their microporous crystalline structure, these zeolites are also uniquely suited to the role of adsorbents. Various forms of zeolites including zeolite A (3A, 4A and, 5A), Faujasites (X and Y) and Pentasils (ZSM-5 and Silicalite) have been used as commercial adsorbents [6]. However, the use of zeolite adsorbents for the sorption of volatile compounds has been covered only to a limited extent in the literature [7, 8, 9, 10].

The primary aspect of this study was the investigation of zeolite adsorbents, mostly of the ZSM-5 type for their CVOC sorption properties, particularly the sorption of trichloroethylene (TCE), the CVOC of principal interest. Detailed studies were conducted to: (i determine the effect of water vapor on TCE capacities of cation exchanged zeolites, (ii) determine the effect of presorbed $MeCl_2$ (methylene chloride), CCl_4 (carbon tetrachloride), and water molecules on dry TCE sorption and (iii) determine the effect of exchanged cations on humid TCE sorption. Results showed that, due to the competitive adsorption of water, the adsorption of TCE decreased significantly. While the presence of presorbed CVOC did not affect subsequent TCE sorption, the dry TCE capacity of chromium-exchanged H-ZSM-5 (henceforth referred to as Cr-ZSM-5) was considerably reduced with water presaturation of the sorbent. The presence of different exchanged cations in the zeolitic structure did not affect humid TCE sorption levels excep with cobalt-exchanged H-ZSM-5 (henceforth referred to as Co-ZSM-5) where a significant decrease was noticed.

In an effort to understand the preferred packing positions of CVOC molecules in Cr-ZSM-5, the interactions of CVOC molecules with the channels and the intersections have been calculated using a simplified Lennard-Jones (12, 6) approach. Using this approach, energetically favored sites (i. e., channels and/or intersections) for the CVOC molecules have been quantified.

In commercial applications, CVOCs are often present in a humid stream where the adsorption of CVOCs is negatively affected by the adsorption of water. A second aspect of this study was an effort to reduce the adsorption of water and enhance the pickup of TCE on zeolites of the Y and ZSM-5 type by subjecting them to silicon chloride ($SiCl_4$) vapors at high temperatures to selectively remove aluminum from the zeolitic framework without significant loss of crystallinity. Sorption results using CCl_4 and TCE show that partial dealumination of Y or ZSM-5 zeolites often creates a medium with significant increase in CVOC sorption and decrease in water pickup at ambient temperature. Furthermore, catalytic activity after dealumination (especially with the Y zeolites) for CVOC destruction is improved.

Also documented in this paper is the performance of Cr-ZSM-5 as a dual-function medium, utilizing both its sorption (low temperature) and catalytic (high temperature) properties. Considerable energy savings can be obtained in such a dual-function process as documented herein for the sorption and destruction of a low concentration level (~110 ppm) TCE stream.

EXPERIMENTAL

Preparation of Cation Exchanged Sorbents:

ZSM-5 samples in the protonated form (silica/alumina (SiO_2/Al_2O_3) =32) were used in the shape of 1/16 in. (0.16 cm) extrudates from UOP. All ZSM-5 samples obtained in the extrudate form contained 20 wt% alumina binder. These zeolites were sometimes used as received but more generally were cation exchanged with transition metals. Cr-ZSM-5 was prepared by exchanging H-ZSM-5 (hydrogen-exchanged ZSM-5) with 0.03 M chromium nitrate solution at 80 °C for 72 h at a pH of 4. Palladium-exchanged H-ZSM-5 (henceforth referred to as Pd-ZSM-5) and Co-ZSM-5 were prepared by exchanging H-ZSM-5 with 0.003 M solution of tetraaminepalladium nitrate (II) and 0.07 M solution of cobalt nitrate, respectively. The times, temperature, and pH for these exchanges were similar to the one described above. After the exchanges, all the sorbent s were thoroughly washed, dried initially at 90 °C for 2 h, then at 200 °C for 2 h, and later calcined at 500 °C for 8-10 h.

Sorbent/catalyst media were characterized for their BET (Brunauer-Emmett-Teller) surface areas using a Quantasorb Jr. and their silica, alumina, and cation contents using a Philips PV9550 X-ray Fluorescence Spectrometer (XRF). The properties of the sorbent/catalyst media are given in Table 1.

Preparation of Dealuminated Sorbents/Catalysts:

Specific Y and ZSM-5 type zeolite samples were partially dealuminated by exposure to $SiCl_4$ vapors under controlled conditions. The $SiCl_4$ treatments were carried out in a fixed bed, quartz reactor (2.0 cm o. d., 1.8 cm i. d.) heated by a Lindberg 55035 hinged-tube furnace with an Omega 6100 temperature controller.

Table 2 documents the operating conditions employe during $SiCl_4$ treatment for both Y and ZSM-5 type zeolites. The dealuminated samples in Table 2 were named according to the number of remaining framework aluminum atoms per unit cell. To prepare these samples the ammonium form of the zeolites was first preheated to about 50 °C above the bed temperature as listed in Table 2 for 3 h in a nitrogen atmosphere. The bed was then brought to operating temperature and subsequently contacted with $SiCl_4$ vapors formed by bubbling nitrogen at ambient temperature through liquid $SiCl_4$ for a specified period. The pellets were then thoroughly washed with distilled water, dried at 80 °C for 4 h, and calcined at 500 °C for 8 h.

The silicon/aluminum (Si/Al) ratios and framework aluminum atoms of the zeolites were determined by the infrared spectra of O-T-O bonds (where T = Si or Al) in the vibration regions according to the empirical equation reported by Sohn et al. [12]. The crystallinities of the modified zeolites were evaluated by measurements of X-ray diffraction patterns (Philips PW 1710 X-ray diffractometer with CuKα radiation).

Sorption, Catalytic, and Dual Function Experiments:

Ambient temperature sorption experiments were carried out in a tubular flow reactor (2.0 cm o. d., 1.8 cm i. d., and approximately 1 m in length) converted to sorption use. CVOC sorption capacities of the sorbent media were measured under either dry or humid conditions. Influent and effluent stream CVOC contents were analyzed using a HP 5970A gas chromatograph (GC) with a 5970B mass selective detector (MS). Saturation was defined as the point where the inlet and outlet concentrations merged. Following the end of each run, sorbents were regenerated in air at 400 °C for approximately 4 h.

Sequential adsorption runs were carried out in three steps: (i) Compound A (CVOC or water) was sorbed on the sorbent until saturation and the sorbent regenerated at the end of the run, (ii) Compound B (CVOC or water, different from Compound A) was presorbed on the sorbent until saturation, and (iii) Compound A was sorbed again on the sorbent (which was now presorbed with Compound B). CVOC concentrations of desorbing Compound B and of adsorbing Compound A in the gas stream were periodically monitored except when water was the desorbing compound. Because of analytical limitations, the concentrations of water in the effluent stream could not be monitored.

Catalytic conversion during CVOC destruction was also measured in the same fixed bed Pyrex reactor described above except that two Lindberg Model 55035 tube furnaces (equipped with Omega Series 6100 temperature controllers) were used to heat the reactor. The GC/MS again provided analysis of most reactants and products. Dräger tubes were used for chlorine (Cl_2), carbon monoxide (CO), and phosgene ($COCl_2$) analyses. Hydrochloric acid (HCl) analysis was done by absorption of the effluent stream into an overhead aqueous solution followed by pH measurement using a Corning 255 ion analyzer.

Experiments involving both sorption and catalysis were carried out in a fixed bed Pyrex reactor shown, in Figure 1. A small separation between the two regions was necessary to facilitate concentration measurements and regulation of temperature. Initially, both the regions were maintained at ambient temperature (23 °C) and a mixture of CVOC, air, and water vapor (approximately 14000 ppm) at a space velocity of 2400 h^{-1} was passed through the system. CVOC and carbon dioxide (CO_2) concentrations at both the bottom and middle sampling ports were periodically measured. At the onset of breakthrough in the lower region, the upper catalytic region was heated to reaction temperature (usually 350 °C) which was followed by slow ramping (5 °C/min) of the lower region to facilitate controlled desorption of CVOC. Desorbed vapors were then catalytically oxidized in the upper region where oxidation products exited the top of the reactor. Following the first cycle, the lower region was cooled to ambient temperature to again act as a sorbent, at which time the upper bed was also allowed to cool. In this manner the system was cycled repeatedly for continuous operation.

RESULTS AND DISCUSSION:

CVOC SORPTION AND CATALYTIC STUDIES

Pure Component CVOC Sorption. A schematic of the unit cell of ZSM-5 is shown in Figure 2. Figure 3 shows pure component sorption of three CVOCs, CCl_4, $MeCl_2$, and TCE on Cr-ZSM-5 at ambient temperature (23 °C). Expressed in terms of the number of molecules per unit cell, these results correspond to 3.2, 6.1, and 6.4 for CCl_4, $MeCl_2$, and TCE, respectively, at saturation. Since TCE (3.2 °A) and $MeCl_2$ (4.5 °A) molecules are much smaller than the free diameter of ZSM-5 (~5.5 °A), these molecules are able to adsorb in the smaller sinusoidal and/or straight channels (see Figure 2). The interaction of these CVOC molecules with the walls of the zeolite plays an important role in determining the preferred packing positions of these molecules; an estimate of these interactions was attempted and is described in the next few paragraphs.

The interaction between the CVOC molecules and the ZSM-5 zeolite framework can be estimated by calculating the Lennard-Jones (12, 6) potentials using a highly simplified method described in detail by Xiao and Wei [13]. Strictly speaking, the Lennard-Jones (12, 6) approach can be applied only to nonpolar molecules, but in practice is also used for polar molecules [14]. This approach has been used by us both for nonpolar molecules (CCl_4) and for polar molecules (TCE: 0.9 debyes, $MeCl_2$: 1.8 debyes, and H_2O: 1.8 debyes).

If the potential energy is attributed to the interactions between the adsorbate molecule and the oxygen atoms only, then the Lennard-Jones interactions at the channels and intersections can be estimated using the equations:

$$\phi_c \approx \sum_{\text{O at channel}} 4\epsilon\left\{[\sigma_c/r_c]^{12}-[\sigma_c/r_c]^{6}\right\} \qquad (1)$$

$$\phi_i \approx \sum_{\text{O at intersection}} 4\epsilon\left\{[\sigma_i/r_i]^{12}-[\sigma_i/r_i]^{6}\right\} \qquad (2)$$

where ϕ_c and ϕ_i are the potentials at the channels and intersections summed over the number of oxygen atoms at these locations; d_m is the minimum kinetic diameter of the molecule, σ_m is the Lennard-Jones length constant; r_c and r_i are the distances from the center of the channels and intersections to the nuclei of oxygens; and σ_c and σ_i are potential length constants for each molecule-oxygen pair at the channels and intersections, respectively.

The values of σ_c, r_c, σ_i, and r_i can be calculated using equations specified by Xiao and Wei. The values of d_m and σ_m for CVOC and water molecules which are needed to estimate the values of σ_c, r_c, σ_i, and r_i are given in Table 3 along with the resultant values of ϕ_c and ϕ_i.

Because of their significantly higher interaction at the intersections, CCl_4 molecules are energetically favored in these regions, whereas, for $MeCl_2$ and TCE, both the channels and the intersections are equally preferred because of almost similar interaction potentials. This preference has been established in the literature by Mentzen [17] who, in his investigation of the structural correlations between the framework symmetry of ZSM-5 materials and the location of various sorbed molecules, proposed the location of CCl_4 molecules at the intersections using powder diffraction data.

As mentioned previously, the Lennard-Jones (12, 6) approach discussed above is highly simplified since it omits polar effects. For polar molecules, the Stockmayer (12, 6, 3) potential is more popular and is recommended [18], but has not been used here because of the unavailability of certain parameters.

Effect of Water Vapor on TCE Sorption:

TCE was the CVOC of primary interest in this study; hence, we decided to investigate its sorption characteristics in detail. The competitive effect of water vapor on the adsorption of TCE on Cr-ZSM-5 is shown in Figure 4. A significant drop, from 6.2 to 2.7 TCE molecules per unit cell, is observed when water, at ~14000 ppm, is present in the feed stream. Also shown in the figure is the effect of preadsorbed water vapor on the adsorption of dry TCE by Cr-ZSM-5. The number of molecules of TCE per unit cell drops from 6.2 to 3.9 when Cr-ZSM-5 is presaturated with 0.08 g of water/g sorbent. These results demonstrate that, due to the competitive adsorption of water, the sorption of TCE, although preferred, is substantially lowered on Cr-ZSM-5. These results are similar to those obtained by Otto et al. [19] who also observed a significant drop in propylene adsorption on Silicalite when water was added in the feed.

When the water concentration is dropped from ~14000 to about ~2000 ppm, the capacity for TCE, at a feed concentration of ~900 ppm, increases significantly to approximately 0.12 g TCE/ g sorbent as shown in Figure 4, while water capacity decreases to 0. 04 g water/g sorbent. The reason for this is that, at the initial stages of competitive adsorption, there is enough room to accommodate both TCE and water so that both these molecules have equal access to the adsorption sites and are adsorbed without interfering with each other. It would seem that at this initial stage, TCE is adsorbed at the preferred packing positions (channels or intersections) while water goes to similar sites that remain available.

Effect of Preadsorbed CVOC on TCE Sorption:

In other sequential adsorption runs, Cr-ZSM-5 was also presaturated with $MeCl_2$ or CCl_4, followed by the adsorption of dry TCE; the results are summarized in Table 4. The values given in parentheses in the fifth column of the table are the capacities for TCE on Cr-ZSM-5 in the absence of any presaturation. Unlike with water, the presaturation of Cr-ZSM-5 with either of these solvents did not significantly affect the subsequent sorption of TCE. However, when TCE was adsorbed on a $MeCl_2$ presaturated Cr-ZSM-5, all of the presaturated $MeCl_2$ was desorbed from the sorbent which would suggest the displacement of $MeCl_2$ from the adsorption sites by TCE. On the other hand, only about 50% of the preadsorbed CCl_4 was displaced by TCE.

Since both the channels and the intersections are preferred by TCE molecules, it is probable that some of the presorbed CCl_4 molecules at the intersections are displaced by TCE. Although the interaction for CCl_4 is significantly higher than that for TCE at the intersections (see Table 3), TCE molecules are adsorbed more strongly because of strong specific interactions (i.e., strong electrostatic interactions resulting from dipole and induced dipole interactions with the adsorption sites and/or cations). Due to this strong adsorption of TCE, the affinity of the surface for CCl_4 molecules decreases, causing it to be partially displaced from its preferred adsorption sites.

Effect of Exchanged Cations on Dry and Humid TCE Sorption:

Summarized in Table 5 are the humid TCE adsorption capacities on ZSM-5 zeolites containing four exchanged cations, namely H, Cr, Pd, and Co. Also shown in the table are values for TCE adsorption capacities in the absence of any water on Silicalite, H-ZSM-5, and Cr-ZSM-5. No consistent trend is noticed with these sorbents except that, comparing dry TCE sorption capacities on H-ZSM-5 and Cr-ZSM-5, a small decrease in TCE capacity (~13%) was observed with Cr-ZSM-5 probably because of the modest chromium ion content in the unit cell (0.63 Cr^{+3}/unit cell). Likewise, from the humid TCE adsorption capacities mentioned in the table, the TCE capacity dropped by about 20% going from H-ZSM-5 to Cr-ZSM-5. While there was no appreciable change between the capacities on Cr-ZSM-5 and Pd-ZSM-5 (~0.06 g TCE/ g sorbent), the drop in TCE capacity on Co-ZSM-5 was about 50% compared to that of H-ZSM-5.

The effect of the cation on sorption [20] depends on (i) the location of these cations, (ii) the size of the cations, and (iii) the nature of interaction between these cations and adsorbate molecules. From the values of cation sizes shown in Table 1 and from the TCE sorption capacities shown in Table 5, no consistent trend can be established based on the sizes of the cations. Due to the small size of TCE molecules, steric hindrance caused by the presence of cations in the structure may not be a factor, and hence, TCE molecules would still have easy access to the adsorption sites. It is interesting to observe that the pickup of water vapor in the experiments on cation-exchanged sorbents remained the same at nearly 0.08 g/g sorbent. This would suggest that the drop in TCE capacity on Co-ZSM-5 was not due to the increased pickup of water (in which case, TCE pickup would decrease due to competitive adsorption). An in-depth study of the nature of interaction between the cations and TCE molecules may be necessary to provide an answer to this.

CVOC Conversion Characteristics:

Reported in Figure 5 are the catalytic conversion characteristics of Cr-ZSM-5 in the destruction of TCE at various temperatures. Also shown in Figure 5 are the conversion characteristics of Cr-Y, another excellent catalyst for the destruction of TCE. Table 6 lists the selectivity of these two catalysts towards the deep oxidation products, HCl and CO_2, during the destruction of TCE.

The selectivity for both the catalysts was largely towards the formation of CO, CO_2, and HCl, although significant and undesired Cl_2 (up to 100 ppm) was found at temperatures above 300 °C. An increase in the amounts of Cl_2 produced for both these catalysts at higher temperatures could be attributed to the Deacon reaction ($4HCl+O_2 \rightarrow 2Cl_2+2H_2O$), which is favored at high temperatures. The formation of CO suggests a series mechanism to produce CO_2, which becomes relatively ineffective at low temperatures.

DEALUMINATION STUDIES

The physical properties of both as-received and partially dealuminated Y and ZSM-5 zeolites are documented in Table 7. The reduction in framework aluminum for the partially dealuminated zeolites resulted in moderate losses in crystallinity (< 40% in characteristic peak intensities) and surface areas (< 25%). Although $SiCl_4$ treatment under controlled conditions can produce a dealuminated sample without significant loss in its surface area [21], conditions in the present study were sufficiently harsh to cause some loss of structure.

Table 8 shows the water and TCE sorption properties of the as-received and dealuminated Y and ZSM-5 zeolites. For dealuminated Y zeolites, whose final framework aluminum content remained greater than 22 per unit cell, there were no significant changes in the TCE and water saturation capacities. Conversely, when framework aluminum was reduced from 51 to 9 per unit cell, an 80% decrease in water saturation capacity and 62% increase in TCE saturation capacity occurred. Similarly, for ZSM-5 zeolite, a reduction in framework aluminum from 5.6 to 1.9 per unit cell yielded a 73% decrease in water sorption and an 81% increase in TCE sorption capacity. The adsorption and selectivity values between these zeolites and CVOCs depend mainly upon interactions of sorbate molecules with the sorbent which, in turn, involve both van der Waals and electrostatic forces. Van der Waals forces occur between any sorbate and any surface, depending on surface geometry, whereas electrostatic forces depend on the polar nature of the adsorbent and adsorbate [22]. In line with our data in Table 8, molecules such as water, with low molecular weight, small size, and high polarity, would have strong electrostatic interactions with the cations of a polar adsorbent and therefore would have high saturation capacities when surface cation concentrations are high, drastically reducing the adsorption of other molecules (TCE, etc.) on the surface due to steric hindrance and competition for the adsorption sites [23]. Vansant [24] further suggested that the strong interactions between the zeolite cation and the dipole moment of the polar molecules produce a diffusion block by clustering the polar molecules around the exchangeable cations in the zeolite channels. With a reduction in surface cation concentration, as occurs with partial dealumination, one would anticipate that sorption of small, high polarity molecules would diminish, while uptake of larger less polar molecules (which depends on non-specific van der Waals forces) would remain unaffected or even increase as steric hindrance and site competition are reduced. This is confirmed by the water and TCE saturation capacity results shown in Table 8 for both Y and ZSM-5 type zeolites, where significant losses in water uptake and significant gains in TCE uptake are noted after partial dealumination of the parent zeolites. The constant water saturation capacities observed in the Y zeolites with Si/Al ratios < 5.2 (shown in Table 8) are due to the limited availability of pore volume to the water molecules as suggested in the literature [25, 26]. Thus, until the site concentration diminishes to 9 per unit cell (in the present study), water pickup is limited by pore volume, not by the number of sites.

Figure 6 shows the CCl_4 catalytic conversion properties of various dealuminated zeolites (Y and ZSM-5 type) measured at different temperatures. At temperatures above 250 °C, all the dealuminated zeolite samples showed essentially complete conversion of CCl_4. However, at 150 °C, Y-D" showed approximately double the CCl_4 conversion compared to Y, whereas ZSM-5 showed less than half the conversion compared to ZSM-5-D.

This may be explained by noting that, following $SiCl_4$ dealumination, the framework aluminum atoms in the zeolite structure are partially replaced by silicon atoms which increase the spacing between neighboring aluminum atoms, further strengthening the remaining Brönsted sites [27, 28]. Since most of the oxidation reactions are catalyzed by proton transfer from the Brönsted sites to the adsorbate molecule, the strength of the acid sites may have a dominant effect in the catalytic activity. This is consistent with results of Broekhoven et al. [29] who investigated the catalytic properties of a series of $SiCl_4$ dealuminated Y zeolites and found a significant increase in the catalytic properties for samples with Si/Al > 15 which is consistent with our improved Y-D" conversion results in Figure 6. Conversely, partial $SiCl_4$ dealumination of as-received ZSM-5 (with an original Si/Al ratio of 16) to ZSM-5-D (with a Si/Al ratio of 48.5) caused a decrease in catalytic activity. The most likely reason for this is that, even though remaining Brönsted sites are strengthened by this process, the final population of these sites in ZSM-5-D is just too small to maintain previous conversion levels.

DUAL-FUNCTION (SORPTION/CATALYSIS) STUDY

Based on its acceptable CVOC sorption capacities and excellent CVOC catalytic conversion, Cr-ZSM-5 was chosen as the medium for dual-function experiments. In order to use Cr-ZSM-5 as a dual-function medium in a low TCE concentration level dual-function process, it was necessary to determine the TCE sorption capacities at low concentrations (<300 ppm). Figure 7 gives the sorption isotherm of TCE in the presence of water vapor at 23 °C on Cr-ZSM-5. The drop in TCE pickup from 0.06 g TCE/g sorbent at ~1000 ppm to 0.03 g of TCE/ g sorbent at ~95 ppm is considered reasonable, especially since the presence of water vapor was significant.

The concept of dual-function runs, where both sorption and catalytic properties are utilized, was described in an earlier section of this paper. Reported in Figure 8 is a dual-function run carried out with a low concentration of TCE (~110 ppm) in the feed stream which had a total sorption/destruction cycle time of 1425 mins. Note that the system operates at ambient temperature except for the short period of desorption and catalytic destruction when the system operates at higher than ambient temperatures. If we define relative energy efficiency as the percentage of cycle time during which the system is unheated, then with a system heating time of approximately 100 mins, the relative energy efficiency is 93%. Since most commercial applications are for treating vapor streams below this concentration level, energy consumption and subsequent operating costs could be substantially lowered compared to those for continuously heated catalytic or non-catalytic systems currently in use.

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Table 1: Properties of Various Sorbent/Catalyst Media

Sorbent/ Catalyst	Surface Area (m^2/g)	Cation Content* (wt%)	Percent Exchange (%)	Number of Cations/unit cell	Ionic Radius of Exchanged Cation [11] (${}^0A$)
H-ZSM-5	366	0.00	0	4.8	0.00
Cr-ZSM-5	328	0.66	40	0.6	0.63
Co-ZSM-5	363	1.20	46	1.1	0.72
Pd-ZSM-5	356	2.20	57	1.3	0.80

* as oxide determined by XRF

Table 2: Tabulation of the Operating Conditions During $SiCl_4$ Dealumination

Sorbent/ Catalyst	Operating Conditions (Temp., Time, Space Velocity)
Y	untreated
Y-D	525 °C, 180 min, 75 h^{-1}
Y-D'	600 °C, 180 min, 75 h^{-1}
Y-D"	600 °C, 180 min, 150 h^{-1}
ZSM-5	untreated
ZSM-5-D	750 °C, 30 min, 75 h^{-1}

Table 3: Lennard-Jones Parameters and Potentials for CVOC and Water Molecules

Molecule	d_m (°A)	σ_m (°A)	ϕ_c (kJ/mol)	ϕ_i (kJ/mol)
TCE	3.2§	3.2*	-6.9	-6.2
$MeCl_2$	4.5§	4.9#	-15.5	-25.2
CCl_4	5.4§	5.9#	-8.3	-50.9
H_2O	2.6	2.6#	-3.9	-3.3

* assumed value; no literature value available

§ from ref.15

from ref. 16

Table 4: Effect of Preadsorbed CVOC on TCE Sorption on Cr-ZSM-5

Sorbent	Concentration of Preadsorbed Compound (ppm)	Molecules/unit cell of Preadsorbed Compound	TCE Concentration (ppm)	Molecules/unit cell of TCE Sorbed	Molecules/unit cell of Preadsorbed Compound Remaining
Cr-ZSM-5	$MeCl_2$/ ~ 1100	6.1	~ 1100	6.1 (6.3*)	0.0
Cr-ZSM-5	CCl_4/ ~ 1600	3.5	~ 1600	7.3 (7.3#)	1.7

* determined at TCE concentration of ~ 1200 ppm in the absence of presaturation

determined at TCE concentration of ~ 1600 ppm in the absence of presaturation

Table 5: Humid TCE, Dry TCE, and Water Pickups on Various Sorbents

Sorbent	Average TCE Concentration (ppm)	Average Water Concentration (ppm)	TCE Pickup (g TCE/ g sorbent)	Water Pickup (g H_2O/ g sorbent)
Silicalite*	1100	0	0.142	0
H-ZSM-5	1190	0	0.164	0
Cr-ZSM-5	1220	0	0.145	0
H-ZSM-5	1050	13000	0.079	0.087
Cr-ZSM-5	1030	14000	0.062	0.079
Pd-ZSM-5	1030	16000	0.061	0.079
Co-ZSM-5	960	14000	0.040	0.080

* Si/Al ratio of 70

Table 6: Selectivity of Cr-ZSM-5 and Cr-Y Catalysts

Catalyst	Temp. (°C)	CO/CO_2	Cl_2/HCl
Cr-ZSM-5	350	1.0	0.094
	300	1.5	0.013
	275	2.0	0.002
	250	2.0	0.000
Cr-Y	350	2.0	0.110
	300	4.0	0.020
	275	6.0	0.040
	250	11.0	0.000

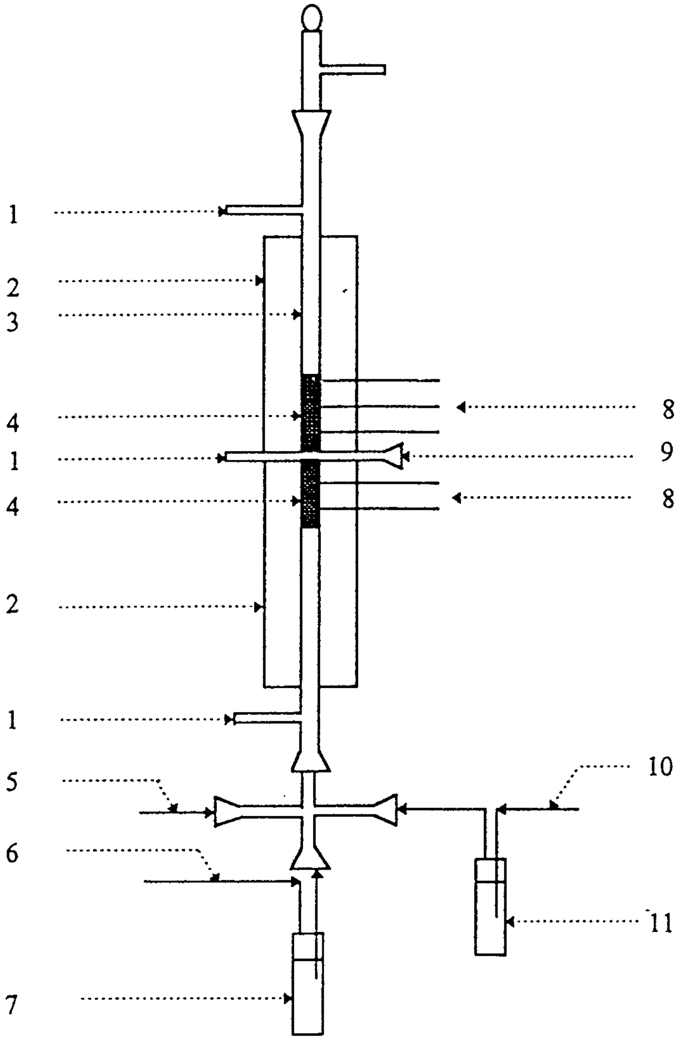
Table 7: Tabulation of Physical Properties of the $SiCl_4$ Dealuminated Zeolites

Sorbent/ Catalyst	Si/Al (atomic)	Framework Aluminum/unit cell	Relative Crystallinity (%)	Surface Area (m^2/g)
Y	2.8	51[a]	100	534
Y-D	5.2	31[b]	80	427
Y-D'	7.7	22[b]	64	441
Y-D"	20.3	9[b]	78	423
ZSM-5	16.0	9[a]	100	395
ZSM-5-D	48.5	3[c]	79	286

a: from manufacturer b: from IR data c: from acidity data

Table 8: Tabulation of Water and TCE Saturation Capacities of Fresh and $SiCl_4$ Dealuminated Zeolites

	Water Saturation Capacity		TCE Saturation Capacity		
Sorbent	Average Water Concentration (ppm)	Moles of Water/g Sorbent ($x10^3$)	TCE Concentration (ppm)	Water Concentration (ppm)	Moles of TCE/g Sorbent ($x10^3$)
Y	13500	11.0	1000	11000	0.55
Y-D	15000	11.2	1000	12000	0.55
Y-D'	10000	10.6	1000	12000	0.49
Y-D"	14000	2.3	1000	12000	1.01
ZSM-5	11500	5.0	1050	14000	0.59
ZSM-5-D	13000	1.3	1300	11000	1.09



(1) Sampling Ports, (2) Tube Furnace, (3) Pyrex Reactor, (4) Dual Function Medium, (5) Main Air Inlet, (6) N_2 to Water Bubbler, (7) Water Bubbler, (8) Thermocouples, (9) Manometer Tap, (10) Air to CVOC Bubbler, (11) CVOC Bubbler

Figure 1: Schematic of Dual-Function Sorber/Reactor

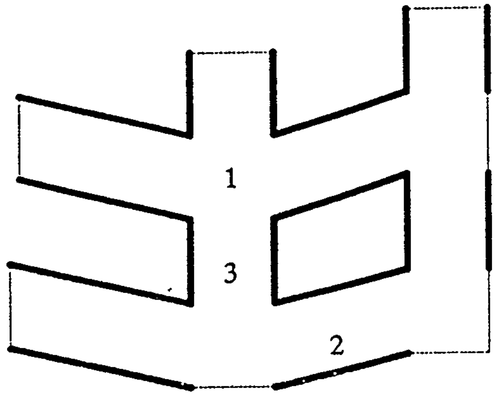


Figure 2: Schematic of a Unit Cell of ZSM-5 Showing Probable Location of Sites (**1.** Intersections, **2.** Sinusoidal Channels, **3.** Straight Channels)

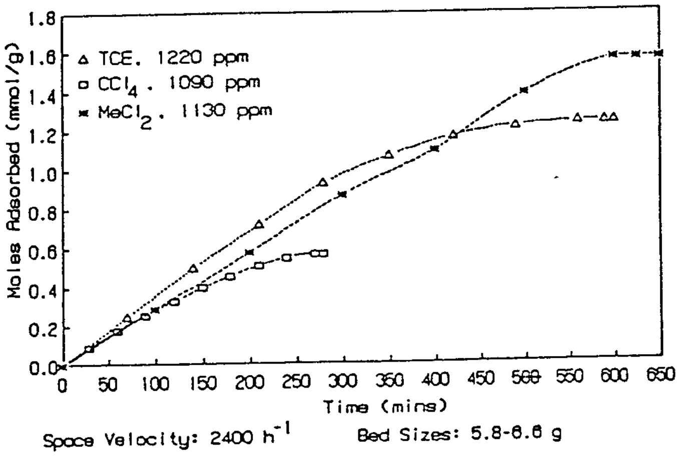
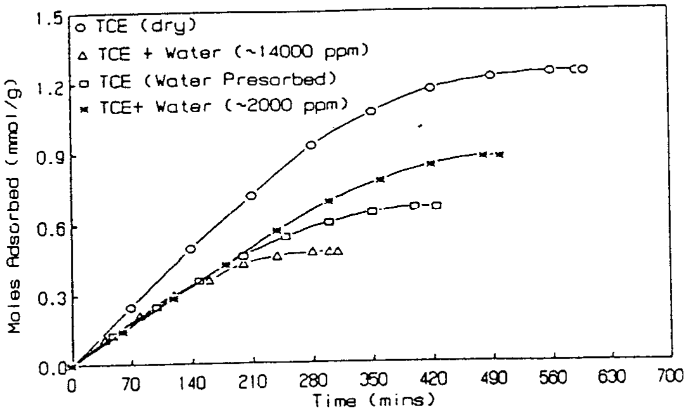


Figure 3: Single Component CVOC Sorption on Cr-ZSM-5 at 23 °C

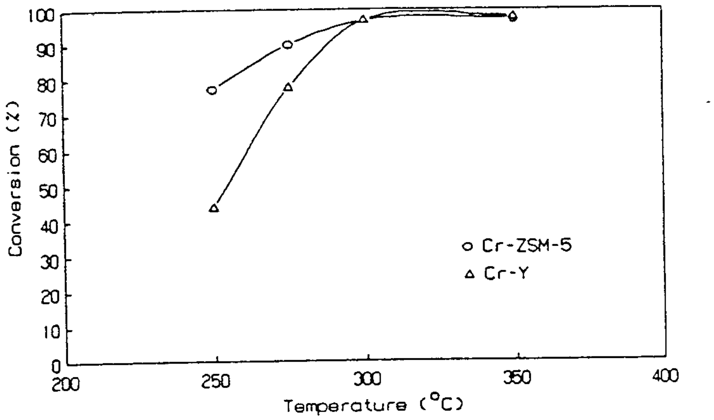


Space Velocity: 2400 h^{-1} Bed Size: 5.8 g

Water Presorbed: 0.08 g/g sorbent (~14000 ppm Water Vapor for 4 h)

TCE Concentration: 950-1220 ppm

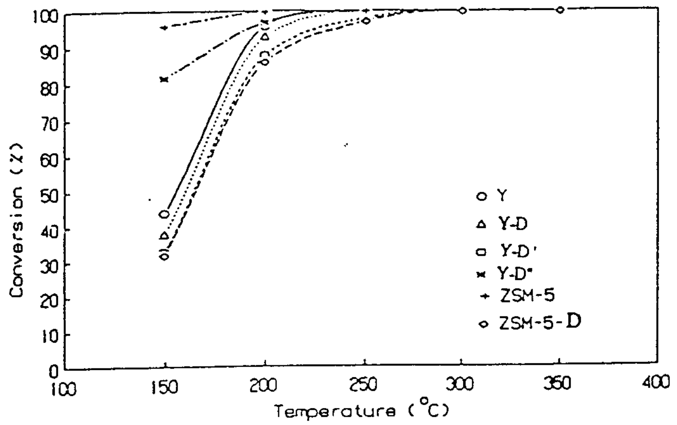
Figure 4: Effect of Water Vapor on TCE Sorption of Cr-ZSM-5 at 23 °C



Space Velocity: 2400 h^{-1} Water Concentration: 14000 ppm

TCE Concentration: 850-1050 ppm

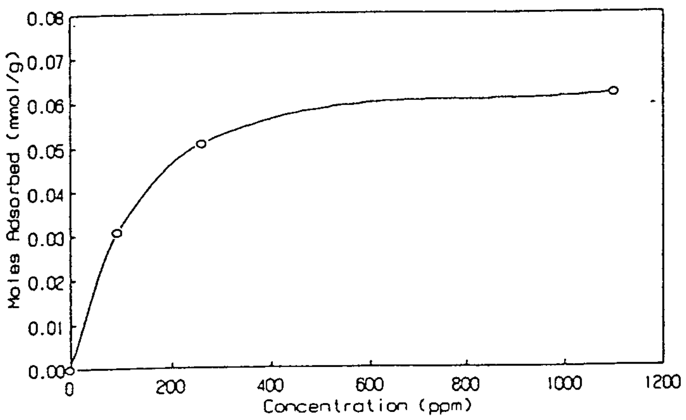
Figure 5: TCE Conversion on Chromium-Exchanged Catalysts



Space Velocity: 2400 h^{-1} Water Concentration: 14000 ppm

CCl_4 Concentration: 1000-1400 ppm

Figure 6: CCl_4 Conversion on Fresh and Dealuminated Zeolites



Space Velocity: 2300 h^{-1} Bed Sizes: 5.8-5.9 g

Water Concentration: 13000-14000 ppm

Figure 7: TCE Isotherm on Cr-ZSM-5 at 23 °C

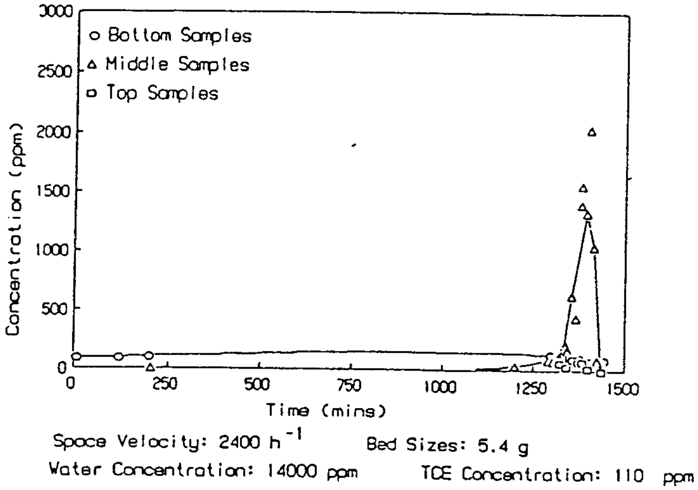


Figure 8: Low TCE Concentration Level Dual Function Process on Cr-ZSM-5