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Energy efficient dual-function sorbent/catalyst media for chlorinated VOC destruction

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Abstract

Several exchanged zeolites (modified Y and ZSM-5) have been developed which are capable of both ambient sorption and elevated temperature catalytic destruction of common chlorinated CVOCs giving rise to an energy efficient process for first storing and later destroying environmentally sensitive solvents.

Keywords: Chlorinated VOC destruction; Zeolites; Energy efficiency

1. Introduction

Current technology for separation and/or destruction of dilute gas phase chlorinated volatile organic compound (CVOC) streams in air generally involves sorption on carbon followed by stripping and recycle or destruction using thermal or catalytic means. Alternatively, the entire stream is heated and the CVOCs continuously destroyed by catalytic or thermal incineration methods. A major disadvantage of these approaches is that they are highly energy intensive [1].

To minimize energy concerns, new dual function zeolite based media which will ambiently physisorb CVOCs and also catalytically oxidize them at elevated temperatures have been developed and studied. The scope of the present study has been to modify both Y and ZSM-5 based zeolites by cation exchange, impregnation and dealumination to produce media which selectively physisorb CVOCs at ambient, and are also hydrophobic, chemically stable and catalytically active for CVOC destruction at temperatures >300°C. The preparation, properties and performance of several zeolites which can accommodate these criteria are outlined herein. Furthermore, a laboratory-scale process utilizing a single zeolite medium has been developed and demonstrated for CVOC sorption and periodic catalytic destruction. Energy efficiencies (defined as percentage of cycle time at ambient temperature) above 90% are easily attainable.

2. Experimental

LZY-84 and ZSM-5 (UOP), 1/16 in. pellets, were utilized sometimes in the acid form as received, but more generally as Cr-exchanged

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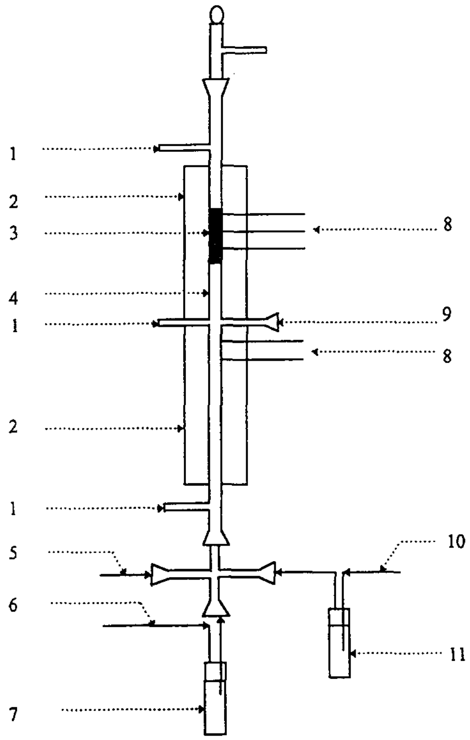

Fig. 1. Schematic of sorption/conversion apparatus. (1) Sampling ports, (2) tube furnace, (3) sorbent bed, (4) pyrex reactor, (5) main air inlet, (6) N_2 to water bubbler, (7) water bubbler, (8) thermocouples, (9) manmeter trap, (10)air to CVOC bubbler and (11) CVOC bubbler.

(0.02 M $Cr(NO_3)_3$ solution, 72 h, 80°C) and/or partially dealuminated ($SiCl_4/N_2$, 3 h, >500°C) prior to experimental use. Results from XRD, XRF, BET and NH_3 TPD confirmed the crystallinity, cation content, surface area and total acidity respectively of the resulting media.

CVOC sorption capacities of the media under either dry or humid conditions were measured at 22°C in a fixed bed 18 mm dia. ID Pyrex reactor as shown in Fig. 1. Analysis of influent and effluent streams for CVOC content was by HP 5890 GC/MS. Saturation was taken as the point where the two concentrations merged.

TCE (trichloroethylene) sequential adsorption runs were also carried out on Cr-ZSM-5. These runs consisted of three phases: (i) sorbing TCE on the sorbent until saturation following which the sorbent was heated to desorb all TCE, (ii) sorbing either water or CCl_4, or $MeCl_2$, on the same sorbent and (iii) sorbing TCE again on the sorbent which is now presaturated with either water or CCl_4 or $MeCl_2$. Concentrations of the desorbing compound and the incoming adsorbate were monitored continuously.

Catalytic activity of the media for CVOC oxidation was measured in the same fixed bed Pyrex reactor except that reactor temperatures were varied between 200–350°C using a Lindberg tube furnace. The GC/MS provided analysis of most reactants and products. CO, Cl_2 and $COCl_2$ analyses utilized MSA tubes (Dräger), while HCl analysis was by absorption into an overhead aqueous solution with subsequent pH measurement (Corning Model 255 Ion Analyzer).

Dual function runs involving both sorption and catalysis were carried out in the tubular reactor setup as shown in Fig. 2. Two Lindberg tube furnaces were employed so that temperatures of upper and lower bed regions could be varied inde-

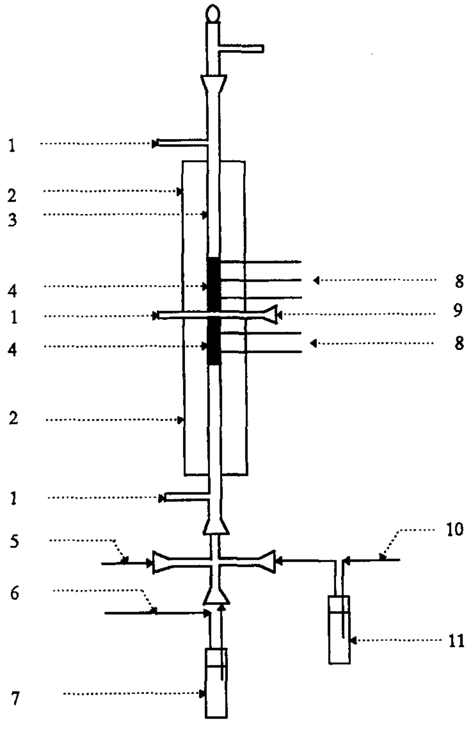

Fig. 2. Schematic of dual-function sorber/reactor. (1) Sampling ports, (2) tube furnace, (3) pyrex reactor, (4) dual-function medium, (5) main air inlet, (6) N_2 to water bubbler, (7) water bubbler, (8) thermocouples, (9) manometer tap, (10) air to CVOC bubbler and (11) CVOC bubbler.

pendently. These runs were carried out by physisorbing trichloroethylene (TCE) from a humid stream at ambient (23°C) temperature. When the bed reached about 50% of its saturation capacity, the upper region was heated to catalytic temperatures (ca. 350°C) followed by slow heating of the lower region to desorb the trapped TCE and water vapor. As the TCE vapors passed upward through the heated catalytic section they were largely converted selectively to CO_2, CO, HCl and small amounts of Cl_2.

3. Results and discussion

The physical properties of two dual function media, H-ZSM-5 and Cr-ZSM-5, are reported below in Table 1.There appeared to be negligible change in surface area, total acidity and peak desorption temperature following chromium exchange. The modest concentration of Brønsted sites in this zeolite, as given by the total acidity, which are primarily of high strength is believed to be the best for combined sorption and catalytic purposes.

Fig. 3 shows ambient temperature TCE sorption on H-ZSM-5 and Cr-ZSM-5 for feeds containing approximately 1000 ppm of TCE with and without water. The chromium exchange of H-ZSM-5 caused a small decrease in TCE saturation capacity (from 1.24 mmol TCE/g sorbent to 1.08 mmol TCE/g sorbent without water, and from 0.60 mmol TCE/g sorbent to 0.47 mmol TCE/g sorbent with water). The modest decrease is thought to be because of the rather low content of chromium in the channel structure of ZSM-5.

Table 1
Properties of the dual function media

Dual function medium	Si/Al	Surface area (m2/g)	Total acidity (g NH3/g sorbent) from TPD	NH3 peak desorption temp (°C) from	Exchanged chromium TPD loading (%)
H-ZSM-5	16	366	0.027	375	0.00
Cr-ZSM-5	16	367	0.025	372	0.49

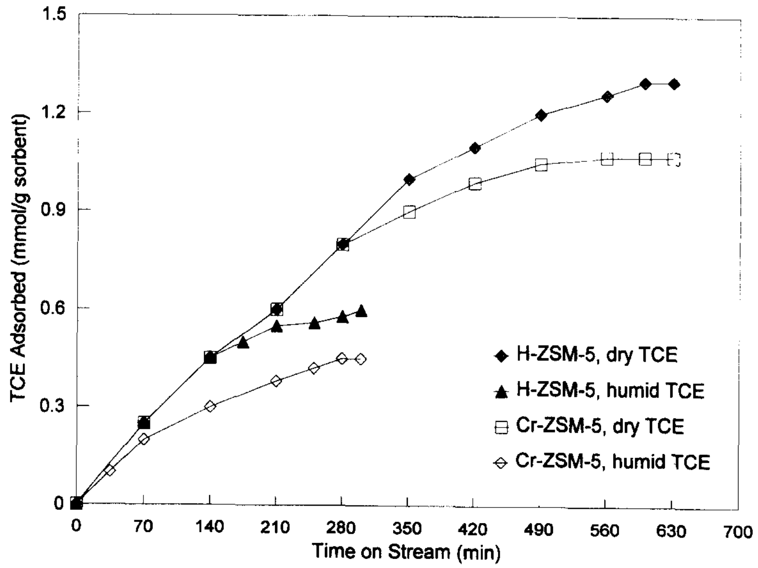

Fig. 3. TCE sorption on H-ZSM-5 and Cr-ZSM-5. Space velocity: 2300–2400 h^{-1}, bed sizes: 5.0–6.1 g and water concentration: 13 000–14 000 ppm.

Table 2
Dry and humid TCE adsorption capacities

Dual function medium	TCE conc. (ppm)	Waterconc. (ppm)	TCE capacity (g/g sorbent)	TCE capacity (mmol/g)	Number of TCE (molecules/unit cell)
H-ZSM-5	1190	0	0.164	1.24	7.2
H-ZSM-5	1050	14000	0.079	0.60	3.5
Cr-ZSM-5	1220	0	0.142	1.08	6.2
Cr-ZSM-5	1050	14000	0.062	0.47	2.7
Cr-ZSM-5	1050	2000	0.115	0.87	5.1

Summarized in Table 2 is the effect of water vapor on the sorption of TCE with ZSM-5 type zeolites. When water (at approximately 14000 ppm) is present in the feed, TCE (at approximately 1050–1200 ppm) capacity dropped significantly from 1.24 mmol/g to 0.60 mmol/g on H-ZSM-5 and from 1.08 mmol/g to 0.47 mmol/g on Cr-ZSM-5. This is due to the competitive adsorption of the sites [2] between water molecules and TCE molecules and also to the water molecules forming clusters around these sites thereby creating a diffusion block for TCE molecules [3]. The preferential adsorption of TCE over water can also be seen by comparing the values listed in the last row of Table 2 with those given in the fourth row of the same table. A drop in concentration of water from 14000 to 2000 ppm nearly doubled the TCE capacity of Cr-ZSM-5 even though TCE concentrations were the same.

The ZSM-5 framework consists of channels (sinusoidal and straight) and intersections [4]. Adsorbate molecules are known to preferentially reside in one or more of these sites. For example, carbon tetrachloride (CCl_4) molecules are known to preferentially occupy only the intersections [5]. A sorbent presaturated with CCl_4 molecules could thus be expected to adsorb a molecule which can occupy the channels. To test these consequences TCE sequential adsorption runs were carried out where Cr-ZSM-5 was presorbed with either CCl_4, water or methylene chloride ($MeCl_2$). Fig. 4 shows the TCE adsorption trend in the presence of a presorbed compound. Also, summarized in Table 3 are the numbers of presorbed molecules/unit cell (uc) displaced by incoming TCE adsorbate molecules in these runs.

As evident from Fig. 4, the adsorption of TCE on Cr-ZSM-5 is strongly concentration dependent in the TCE concentration range 1220 and 1450 ppm. Also, in the presence of a presorbed compound the adsorption of TCE was generally lower and slower except in the case of CCl_4. The slight increase in TCE adsorption with CCl_4 presorption was probably caused by the higher TCE feed concentration (1650 ppm) used during this run. For water and $MeCl_2$, the slower pickups were due to the steric hindrance caused by certain of the presorbed molecules present in the zeolite lattice.

From the values of the number of molecules desorbed/unit cell listed in Table 3, it is apparent that there is competition for the adsorption sites in Cr-ZSM-5. The lower sorption value (3.5 molecules/uc) for CCl_4 suggests that, because of their larger size, these molecules are only able to occupy the larger intersection region sites. Since nearly all of the presorbed CCl_4 molecules were displaced (3.3 of 3.5), it is clear that the intersections are preferentially available for the TCE molecules. Also, since all the $MeCl_2$ molecules were displaced (6.1 of 6.1) from the unit cell, it is probable that TCE and $MeCl_2$ prefer the same types of sites. The lower capacity of Cr-ZSM-5 for TCE when the sorbent was presaturated with water is because of the strong adsorption of water at the cation sites (ion–dipole interaction) which reduces the affinity of the sorbent for the other polar molecules. Also, because of the formation of water clusters around the cation sites, a diffusion block is created which causes a hindrance to subsequent TCE adsorption.

Reported in Fig. 5 is the catalytic behavior of Cr-ZSM-5 for TCE conversion as a function of

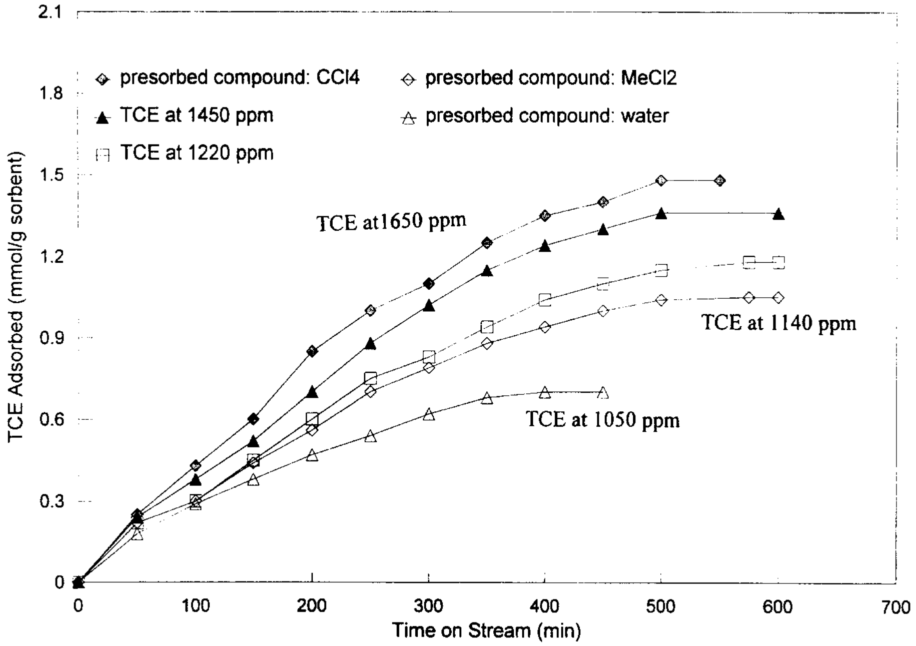

Fig. 4. Effect of presorbed molecules on TCE adsoption. Sorbent: Cr-ZSM-5, space velocity: 2300 h^{-1} and bed sizes: 5.8 g.

temperature. The selectivity was largely towards the formation of HCl and CO_2. Based on its excellent activity and its acceptable CVOC adsorption capacities, Cr-ZSM-5 was chosen as the medium of choice for subsequent runs where both sorption and catalysis were utilized in one continuous dual function run.

4. Zeolite dealumination

It is possible to improve the dual function media performance (i.e., increase its CVOC saturation capacity and/or conversion capability) by selectively modifying the chemical nature of the surface using different treatment procedures such as dealumination, cation loading, realumination, flourination, etc. In the present study the chemical nature of the surface was altered by subjecting the zeolite to $SiCl_4$ vapors under closely controlled conditions which resulted in the partial replacement of the framework aluminum atoms in the zeolite by silicon atoms without significant loss in crystallinity. The drop in the aluminum content would reduce the surface polarity of the zeolite thereby reducing the interaction with highly polar (water) molecules. Table 4 documents the sorption and catalytic conversion properties of both dealuminated (ZSM-5-D and Y-D) and as-received (ZSM-5 and Y) zeolites. The dealumi-

Table 3
Effect of presorbed molecules on TCE adsorption

Sorbent	Presorbed compound/conc. (ppm)	Molecules/uc of presorbed compound	TCE conc. (ppm)	Molecules/uc of TCE adsorbed	Molecules/uc of presorbed compound desorbed
Cr-ZSM-5	water/13000	25.0	1050	3.7	ND[a]
Cr-ZSM-5	CCl_4/1590	3.5	1650	8.5	3.3
Cr-ZSM-5	$MeCl_2$/1100	6.1	1140	6.1	6.1

[a] Indicates not determined.

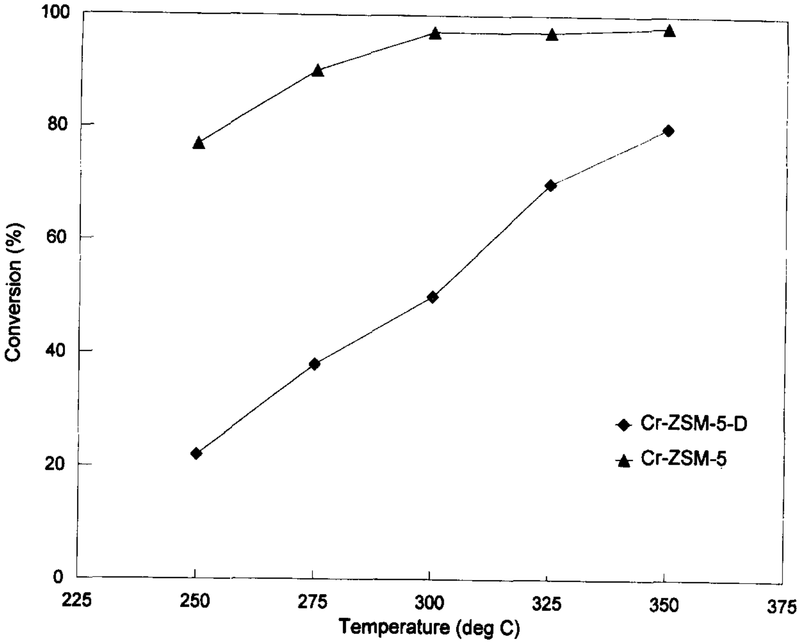

Fig. 5. TCE conversion on chromium exchanged zeolites. Space velocity: 2200–2400 h^{-1}, bed size: 8.1 g and water concentration: 11 000–14 000 ppm.

nated zeolites were chosen from a group of $SiCl_4$ treated samples based on their degree of dealumination and relative crystallinity. Reductions in framework aluminum content after treatment were estimated by changes in NH_3 TPD (acidity) data for the ZSM-5 media. For the Y based media loss of framework aluminum was estimated from structure sensitive IR data. Relative crystallinity was estimated based on changes in peak heights from XRD data.

For ZSM-5, reduction in framework aluminum from 9 to 3 resulted in a 73% decrease in water sorption capacity but also a 65% decrease in CCl_4 catalytic conversion. Conversely, for Y zeolite, a reduction in framework aluminum from 51 to 9 yielded an 80% decrease in water sorption capacity and also an approximate doubling in CCl_4 catalytic activity.

The TCE sorption capacity measured in the presence of water increased by 81% in the case of

Table 4
Dealumination, sorption and conversion characteristics

Zeolite	Framework aluminum per unit cell	Si/Al	Relative crystallinity (%)	Water sorption capacity[a] (g/g sorbent)	TCE sorption capacity[b] (g/g sorbent)	%Conversion	
						CCl_4 (150°C)	TCE (300°C)
ZSM-5	9	16.0	100	0.090	0.079	96	—
ZSM-5-D	3	48.5	80	0.024	0.143	32	—
Y	51	2.8	100	0.198	0.076	38	—
Y-D	9	20.3	80	0.041	0.123	82	—
Cr-ZSM-5	9	16.0	—	0.080	0.060	—	95
Cr-ZSM-5-D	3	48.5	—	—	—	—	52

[a] Saturation capacity measured at ca. 14000 ppm of water, space velocity = 2400 h^{-1}.

[b] TCE saturation capacity at ca. 1100 ppm of TCE and ca. 11000 ppm of water, space velocity = 2400 h^{-1}.

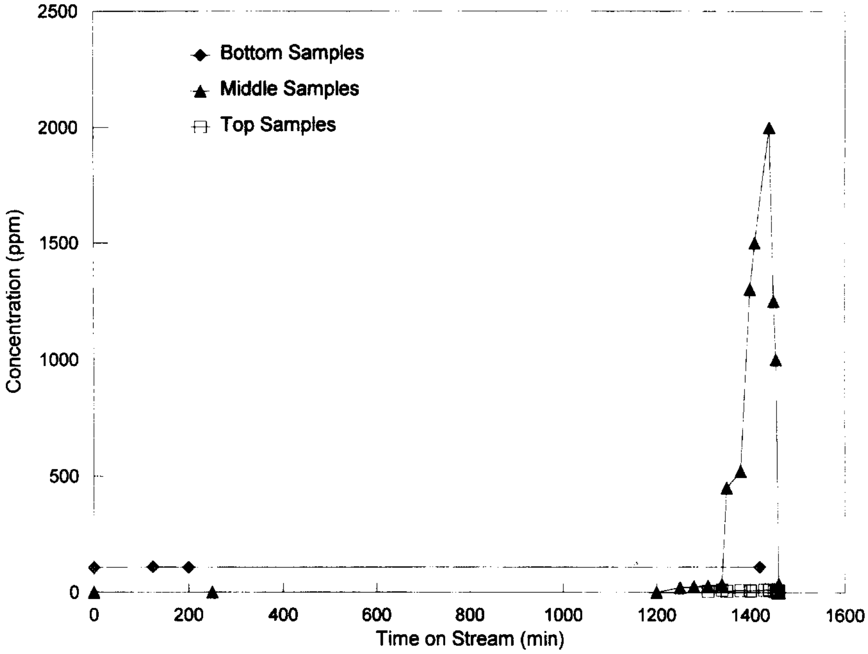

Fig. 6. Low concentration dual function run on Cr-ZSM-5. Space velocity: 2400 h^{-1}, bed sizes: 5.4 g, 5.4 g, water concentration: 14 000 ppm and TCE concentration: 110 ppm.

the ZSM-5-D zeolite and 62% in the case of the Y-D zeolite. The consistent increase in CVOC sorption and decrease in water sorption agrees with the geometrical and surface polarity theories for this phenomenon. The decrease in CCl_4 catalytic activity for ZSM-5-D compared to a corresponding increase for Y-D tells us that the optimum spacing of framework aluminum (the active sites for catalysis) in ZSM-5-D has been exceeded, whereas for Y zeolite it has not. This is reasonable based on the wide difference in Si/Al ratios for the starting ZSM-5 and Y zeolite samples.

Table 4 also shows data for chromium exchanged ZSM-5 and ZSM-5-D (Cr-ZSM-5, and Cr-ZSM-5-D respectively). Chromium exchange greatly enhances the catalyst activity for TCE conversions with no significant changes in water or TCE sorption capacity. In the case of Cr-ZSM-5-D (as with ZSM-5-D and its CCl_4 conversion), TCE activity dropped (from 95% to 52%) after partial dealumination, again telling us that the optimum catalytic spacing for aluminum in Cr-ZSM-5-D has been exceeded.

5. Dual function sorber/reactor experiments

Results from a single cycle of a dual function run (as described in the Experimental section) are shown in Fig. 6. Here a single medium (Cr-ZSM-5) was used to ambiently sorb and then destroy the desorbed TCE. Since thermal energy is needed only during the relatively brief desorption/destruction period (about 100 min out of the 1460 min cycle or only 7% of the run time), energy costs are significantly reduced over continuously heated systems. As inlet CVOC concentrations are further reduced, energy comparisons become even more favorable.

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