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Radiation Induced Catalytic Dechlorination of Hexachlorobenzene on Oxide Surfaces

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Radiation induced catalytic dehalogenation of hexachlorobenzene (HCB) adsorbed to alumina (Al_2O_3), silica (SiO_2), titania (TiO_2), zirconia (ZrO_2), and a commercially available zeolite has been studied using Cobalt-60 (^{60}Co) as a radiation source. Solid-particulate samples were irradiated over a dose range of 0−58 kGy, and the chemical changes were monitored using Fourier transform infrared diffuse reflectance (FTIR-DR) and gas chromatography with electron capture detection (GC-ECD). The extent of HCB degradation on the metal oxides was found to increase dramatically in samples evacuated under vacuum, pointing to the competitive scavenging of conduction band electrons by surface adsorbed species, primarily oxygen. Coadsorbed water diminished HCB conversion on all oxides but to a greater degree on alumina. HCB degradation on metal oxides was found to be highly dependent upon the conduction band energy of the support material, thus confirming the occurrence of ultra-band-gap excitation and charge separation in irradiated oxides. Higher yields of dechlorination products were witnessed in alumina and silica samples. Zeolite, titania, and zirconia were also found to be inefficient in promoting radiation induced catalysis. The absence of oxidation products in the irradiated HCB/oxide samples suggests the inaccessibility of holes to undergo interfacial charge transfer with the organic substrate.

Introduction

The radiolytic degradation of HCB in contaminated soils occurs at higher rates and to a greater extent in low organic, high mineral content soils than in soils having high organic content.[1] To probe the nature of the specific reaction of contaminants adsorbed to natural mineral soils under gamma-radiolysis, alumina was selected as a model soil mineral and the radiolytic transformation of HCB adsorbed to alumina was followed using diffuse reflectance FTIR and GC-ECD. Because alumina has a very large band-gap with a conduction band close to the vacuum level,[2] it can only be activated with high-energy radiation. The results of these experiments showed the occurrence of radiation-induced, ultra band-gap charge separation, followed by the interfacial charge transfer and degradation of adsorbed HCB.[3]

Earlier radiolytic studies with silica and zeolites have shown that ionization events in these solids are similar to those observed in nonpolar media.[4−6] Gamma rays are energetic enough to create electron−hole pairs in wide band gap oxide particles, most of which recombine within first few picoseconds to produce triplet excitons.[5] A fraction of these charge carriers are also trapped at defect sites. There have been numerous studies using ionizing radiation to produce excitations in metal oxide particles with subsequent charge transfer to adsorbed molecules.[3,7−10] For systems of solids with coadsorbed molecules, high-energy radiation will generally excite the solid producing ionization in remote regions of the solid and result in subsequent transfer of excitation energy to the adsorbate.[7,11]

The principle of radiation induced catalysis is similar to that of photocatalysis in which ultraband-gap excitation of oxide particles results in charge separation. These charge carriers, in the conduction and valence bands, recombine or migrate to the particle surface, where they become trapped and/or may participate in the interfacial oxidation and reduction of adsorbed species.[12] In general, the radiolysis of solids with adsorbate produces ionic products and free radicals derived from these ions. In photocatalysis, one employs semiconducting materials with band-gaps less than 3.5 eV. However, in radiation induced catalysis, one can use relatively large band-gap materials (insulators), thus paving the way to use oxides that are present in greater proportions in natural soils. Radiolysis of EDTA solutions containing titania colloids led to a 30% increase in EDTA degradation.[13] In addition, this phenomenon may play a role in the radiolytic processes occurring in radioactive tank wastes containing large amounts of metal oxides and organic compounds at US Department of Energy (DOE) sites.[14] Finally, because gamma rays have large penetration depths in comparison to UV radiation, it may be possible to engineer radiation activated catalysts having high surface areas and redox properties to treat the most recalcitrant pollutants.

A basic understanding of the catalytic properties of representative oxides is therefore useful for developing radiolytic treatment strategies for contaminated soils. We have now carried out steady-state radiolysis of HCB adsorbed on to silica, alumina, titania, zirconia, and zeolite in order to establish the role of different oxide support in catalyzing HCB transformation.

Experimental Section

Sample Preparation. Fumed alumina and titania samples were obtained from Degussa (Akron, OH), HCB and powdered zirconia from Aldrich (Milwaukee, WI), and fumed silica and powdered zeolite from Sigma (St. Louis, MO). These chemicals were of the highest purity available and were used as received

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TABLE 1: Surface Areas of Supports

support	surface area [m^2/g]
Al_2O_3	100^a
SiO_2	255^a
TiO_2	50^a
ZrO_2	50^b
zeolite	200^b

[a] Measured values. [b] Manufacturer reported.

without further purification. In preparing metal oxide samples, a desired mass of HCB was added to a given mass of metal oxide and then thoroughly mixed with acetone and hexane (1:1 v/v). Solvents were then evaporated under nitrogen until the metal oxide solution was reduced to a paste. Subsequently, pastes were allowed to dry in an oven overnight (50 °C). All oxide samples were prepared via the addition of HCB on a mass to mass basis with a normalized amount of 15 mg HCB per total surface area of 100 m^2 to account for differences in the surface areas of various supports. Unless otherwise specified all supports were used as received.

Table 1 above reports the surface area of all the oxide supports used in the present investigation. In the case of zeolite and zirconium oxide, surface areas were determined from methylene blue adsorption experiments.[15] This was accomplished through the Langmuir adsorption isotherm by adding a known amount of methylene blue solution to various amounts of the support. The amount of methylene blue required to achieve monolayer coverage of the support was estimated for determining the surface area of the support.

Individual vials containing approximately 1.0 g of solid sample were irradiated to produce samples for GC measurements. These cells were prepared and irradiated under the same conditions as the FTIR samples. A series of experiments were performed in the absence of oxygen (under vacuum) and in a water-saturated atmosphere. Oxygen was removed from the sample by placing the vial or the holder in a glass cell and connecting it to vacuum line for 15 min prior to irradiation. The evacuated cell assembly was kept in the irradiator for the desired time of exposure. Because four dose periods were used, a given sample was repeatedly (5 times total) evacuated by vacuum after FTIR analysis at each dose interval. GC-ECD (gas chromatograph with Electron Capture Detection) results confirmed that no significant HCB desorption from the oxide samples occurred with the application of the vacuum conditions. For oxides irradiated under a water-saturated atmosphere, samples were initially exposed (30 min) to a water-saturated, nitrogen gas stream within a large glass cell (150 mL).

Gamma Radiolysis. Radiolysis of all samples was performed using a Shepard-109 ^{60}Co source. ^{60}Co is an emitter of high energy, 1.25 MeV, photons (γ-rays). The Shepard-109 is a concentric well type source with a measured dose rate of approximately 243 Gy/min at the time of experimentation. Dose rates were calculated in our laboratory using Fricke dosimetry.[16]

FTIR samples were irradiated within diffuse reflectance sampling cups to prevent variation in the location of samples with respect to the FTIR infrared beam. For vacuum samples, a special glass irradiation cell was constructed to hold FTIR sampling cups. Spectra of individual samples were recorded before and after radiolysis at different time period of irradiation.

Diffuse Reflectance Fourier Transform Infrared (FTIR) Measurements. All FTIR experiments were performed using a Bio-Rad FTS 175, FTIR spectrometer with a diffuse reflectance accessory. Samples were placed within micro sampling cups for analysis inside the instruments and nitrogen was purged through the chamber to prevent interference from CO_2. The diffuse reflectance spectra of all samples were measured in the region 400−4000 cm^{-1} at a resolution of 8 cm^{-1}. No further enhancement in spectral features was observed when the resolution was increased from 8 to 4 cm^{-1}. The measurements were limited to an analytical window of 2000−1200 cm^{-1}.

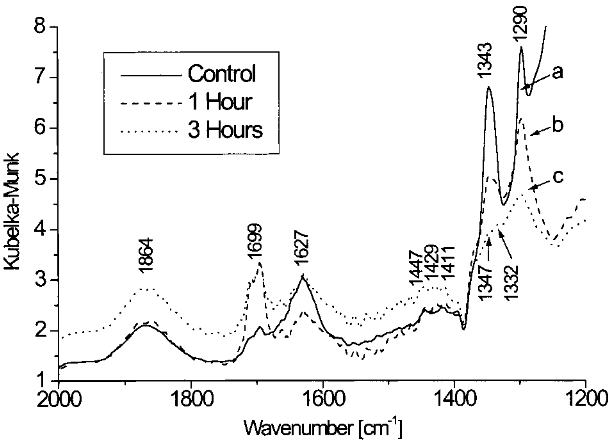


Figure 1. FTIR-DR spectra of HCB on silica (38.25 mg HCB/g) after (a) 0, (b) 1, and (c) 3 h of γ-radiation and under a vacuum (−760 mmHg).

Extraction and Analysis. All samples were analyzed by conventional GC techniques for byproduct analysis and quantification. Compounds bound to metal oxides were extracted in a solution of acetone and hexane 1:1(v/v). An internal standard, 1,3,5-tribromobenzene, was added to adjust responses for changes in volume. This compound was used due to its structural similarity to HCB and high response in electron capture detectors (ECD). After internal standard addition, samples were sonicated for 15 s to enhance desorption of HCB from the oxide surface. Resulting suspensions were then centrifuged for 3 min at 890 × *g* to remove oxide particles from suspension, thus producing a clean sample for injection into the GC interface.

A method for the detection and quantification of HCB and reduced forms of HCB using GC-ECD was established in previous research.[1] Identification of products was verified through the use of a Hewlett-Packard 6890 GC-MS. Mass spectra were compared to NIST databases for tentative identification and confirmed with known standards. For GC-MS work, a J&W Scientific DB-5 column was used with oven programming being identical to that used in GC-ECD work.

Results

^{60}Co Irradiation of HCB/Oxides. In Figure 1, the FTIR spectrum of HCB adsorbed onto silica (Spectrum a) is compared to the spectra of irradiated silica/HCB samples (Spectra b and c) under vacuum. Prior to irradiation (Spectrum a), samples showed two peaks at 1343 cm^{-1} and 1290 cm^{-1}, which can be attributed to the stretching of aromatic C=C bonds in the HCB molecule.[17] This spectrum also showed a weak region (1600−1450 cm^{-1}) of overtone bands from C−Cl bending bands.[17] The region from 1580 to 1500 cm^{-1} is often attributed to commonly adsorbed hydrogen carbonate ions on the surface of alumina particles.[18] Such bands are the result of asymmetric stretching modes of the CO_3^{2-} ion.[19−21] However, it is important to note that because C−Cl overtone bands may also exist in this region, it is not possible to resolve these bands in the present data.

Upon irradiation for an hour (dose of 14.6 kGy) (Figure 1; Spectrum b), the aromatic C=C stretch band found at 1343 cm^{-1} is slightly broadened, decreased in intensity, and formed a

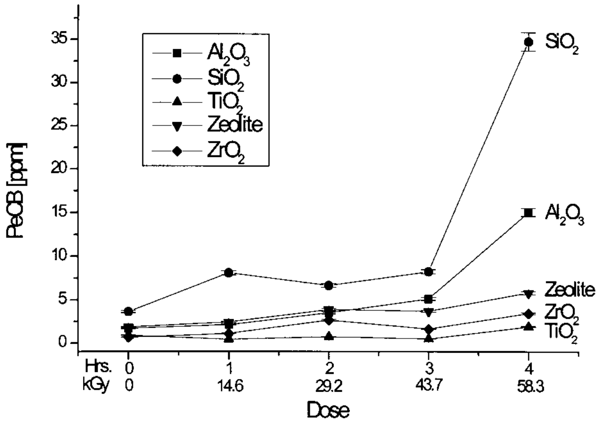


Figure 2. Formation of PeCB on high coverage (a) alumina (■), (b) silica (●), (c) titania (▲), (d) zeolite (▼), and (e) zirconia (◆) as a function of time (dose) under an open atmosphere.

doublet at 1347 and 1332 cm^{-1}. In addition, other aromatic C═C stretch band at 1290 cm^{-1} broadened and decreased in intensity as well. Furthermore, the formation of a conglomerate of peaks at 1447, 1429, and 1411 cm^{-1} could also be seen. Earlier research in our laboratory with HCB adsorbed to alumina has shown that these changes in the FTIR spectra arise from the dechlorinated forms of HCB, primarily pentachlorobenzene (PeCB) and tetrachlorobenzene (TeCB) isomers.[3] The large conglomerate at ~1429 cm^{-1} results from the constructive interference of peaks related to the presence of dechlorination byproducts, which have numerous contributing peaks in the region from 1480 to 1300 cm^{-1}. In a similar manner, changes occurring in the aromatic C═C bands at 1343 and 1290 cm^{-1} are consistent with the formation of PeCB on the oxide surface. Finally, the peak at 1699 cm^{-1} is attributed to the C═O stretching of residual acetone used in sample preparation.

Inspection of the 3-h spectrum (Figure 1 Spectrum c) showed further broadening and decreased intensity of the aromatic stretch bands at 1343 cm^{-1} and 1290 cm^{-1}. In addition, the doublet at 1347 cm^{-1} and 1332 cm^{-1} became distinct and separated after 3 h of irradiation. With increasing radiation dose, we expect to observe an increased amount of transformation of HCB on silica surface. Dechlorination byproduct peaks at 1447, 1429, and 1411 cm^{-1} increased slightly and became more pronounced. However, little change in the peaks at 1699 cm^{-1} and 1627 cm^{-1} was witnessed when compared to the 1 h irradiated spectrum (Figure 1 Spectrum b).

FTIR spectra obtained for all 5 HCB coated oxide samples before and after irradiation under an open atmosphere are included in the Supplementary Information (Figure 1). The 4 h irradiated samples (58.3 kGy) showed spectral changes similar to those found in Figure 1 for HCB coated silica. In the case of zirconia/HCB samples, very little degradation in comparison to the other surfaces was observed. Even at high irradiation doses (160.6 kGy), we could not observe any significant transformations in these samples.

Dechlorination of HCB on Oxides under an Open Atmosphere. In Figure 2, the production of PeCB (extracted and then quantified by GC-ECD) in samples irradiated under an open atmosphere is shown. Results are expressed as mg PeCB per kg oxide (ppm). Overall, the production of PeCB found in the 3 and 4 h irradiated samples was greater in alumina and silica samples. Silica showed greater overall HCB degradation, approximately 2−3 times greater than that on alumina. In contrast, virtually no HCB conversion was found in titania (a negligible 1.5 ppm conversion following 4 h of irradiation) or zirconia samples. Likewise, zeolite samples showed only a marginal HCB conversion. In alumina and silica samples, trace levels of TeCB were also detected pointing to an advanced dechlorination step in these samples.

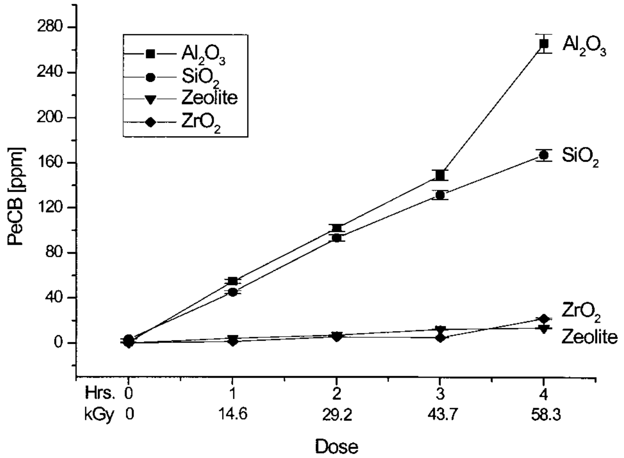


Figure 3. Formation of PeCB on high coverage (a) alumina (■), (b) silica (●), (c) zeolite (▼), and (d) zirconia (◆) as a function of time (dose) under a vacuum.

Dechlorination of HCB on Oxides under Evacuated Conditions. The irradiation of silica and alumina samples under vacuum (10^{-3} Torr) resulted in very large increases in PeCB formation (Figure 3). As compared to the open atmosphere irradiation, the production of PeCB in evacuated alumina samples increased by more than an order of magnitude (18×). Similar enhancement was also observed in evacuated silica/HCB samples. Evacuation of these samples led to 1.6 times more degradation on alumina than on silica, a reversal of the results under an open atmosphere (Figure 2). Although the extent of PeCB formation on ziolite and zirconia increased by small amount (2.35 and 6.41 times, respectively) in comparison to the open atmosphere condition, overall, very limited HCB conversion was observed relative to that on silica or alumina. If the adsorption of surface species such as oxygen or water was the only factor responsible for slower degradation in open atmosphere irradiated samples, we would have seen a similar increased degradation efficiency for all supports. Thus, the choice of oxide as a catalytic support is important in controlling the radiation induced degradation of HCB.

Elevated levels of HCB degradation under vacuum resulted in a likewise increase of TeCB production (Figure 4), for alumina and silica samples. Formation of TeCB was found to increase rapidly as a function of time. Because of limitations in GC separation, only one TeCB isomer (1,2,3,4-TeCB) was quantifiable due to the coelution of 1,2,3,5-TeCB and 1,2,4,5-TeCB.

Effect of Moisture on HCB Dechlorination. The irradiation of samples under a water-saturated atmosphere was performed to determine the effect of surface adsorbed water on HCB degradation. Prior to irradiation, a water-saturated gas stream (nitrogen) was passed through a cell containing the oxide samples for about an hour. Surfaces irradiated under a water-saturated atmosphere (Figure 5) showed an inhibitive effect toward to HCB reduction. Unlike the open atmosphere or evacuated conditions very little degradation occurred at low dose periods. At higher doses, the degradation differed somewhat from the trends observed in Figures 2 and 3. As witnessed in the open atmosphere experiments, HCB degradation in silica samples was better than other supports. For 4 h irradiated silica/HCB and alumina/HCB samples, the extent of degradation in

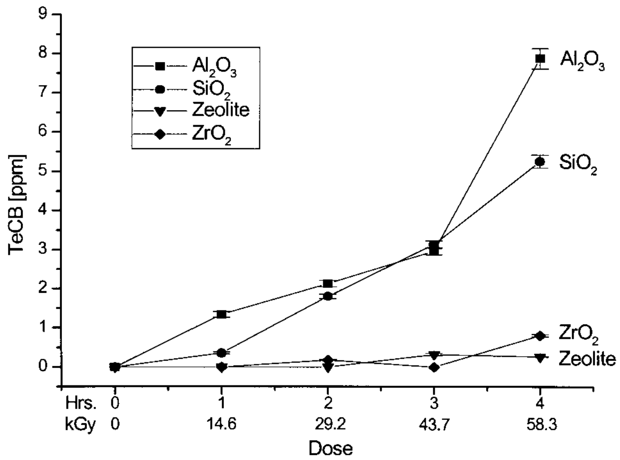


Figure 4. Formation of 1,2,3,4-TeCB on high coverage (a) alumina (■), (b) silica (●), (c) zeolite (▼), and (d) zirconia (◆) as a function of time (dose) under a vacuum.

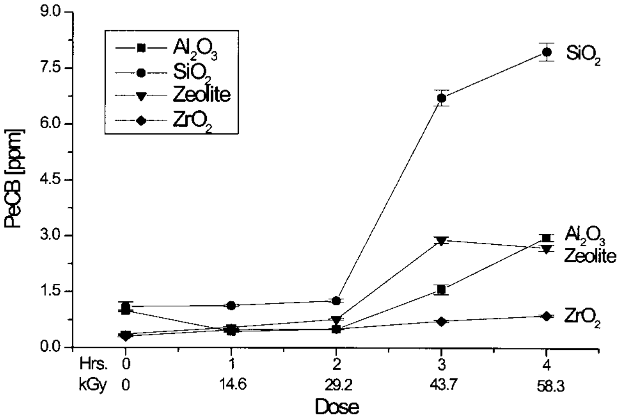


Figure 5. Formation of PeCB on high coverage (a) alumina (■), (b) silica (●), (c) zeolite (▼), and (d) zirconia (◆) as a function of time (dose) under a water saturated atmosphere.

comparison to the open atmosphere irradiation experiments, decreased by a factor of 4−5. Other oxides also showed similar decreased HCB degradation efficiency. These results show that the coadsorbed water on the oxide surface has an inhibitive effect on the HCB degradation.

Yields of HCB Byproducts. The radiolytic transformations of solutes can be quantified in terms of *G* values, defined as the number of molecules formed or lost per 100 eV of energy absorbed.[22] *G* values allow for the direct comparison of pentachlorobenzene (PeCB) yields, at a given dose, between samples of different supports under different atmospheric conditions. Table 2 summarizes the *G* values, or yields, of PeCB when samples are irradiated under an open atmosphere, water-saturated nitrogen atmosphere and in a vacuum for 4 h (58.2 kGy). *G* values are also reported for the formation of 1,2,3,4-tetrachlorobenzene (TeCB) in a vacuum samples.

G values of dechlorinated products (viz., PeCB and TeCB) indicate that the surface adsorbed species (e.g., O_2 or H_2O) influence the course of HCB degradation on irradiated oxide samples. Exclusion of these species by evacuation resulted in maximizing the efficiency of catalytic degradation of HCB on oxide surfaces. Almost 2 orders of magnitude difference exist between the *G* values for samples irradiated on the surface of alumina under a water-saturated atmosphere and vacuum. Similarly, large increases were observed in silica (×21) and zirconia (×16) samples. However, the increase in values of *G* for zeolite samples remained relatively small. Silica was more effective for HCB degradation than the other oxides when the experiment was carried out under ambient or water saturated irradiation conditions. In general, the irradiation of samples under an open atmosphere showed slightly greater PeCB production on all suports when compared to water saturated samples. In particular, alumina samples showed the greatest increase (4.4 ×) in PeCB production when moving from a water saturated to open atmosphere. (2.0×10^{-3} vs 8.8×10^{-3}, respectively).

Discussion

High-energy radiation is known to interact directly with the solid or liquid substrate and induce ionization events. The cross section for absorption of ionizing radiation is directly proportional to the electron density of the irradiated material. In the present experiments, the oxide supports constitute the major fraction (>99%) of the irradiated material. The amount of energy absorbed directly by HCB in a oxide/HCB sample is negligible because the concentration and electron density of the oxide support dominate the irradiated sample. Hence, the incident gamma radiation is deposited into oxide support via electronic interactions. This argument is supported by the observation that negligible HCB transformations occurred in earlier research on KBr[3] and on TiO_2 in the present research when coated with HCB. (Note that these supports do not induce catalytic transformation of HCB and hence serve as reference.)

The oxide supports in the present experiments directly absorb the incident γ-rays and induce charge separation within the oxide material. The electrons produced in the oxide particle are quickly thermalized to conduction band energy level or get trapped at the surface vacancies. Triplet excitons and trapped electrons can also react with surface bound OH groups to generate H atoms via radiolytic homolysis of the hydroxyl group (O−H bond) and dissociative electron attachment to silanol groups.[4,5] Surface adsorbed aromatic species may thus interact with the conduction band electrons or H atoms to undergo reductive dechlorination. In experiments where silica was pretreated at higher temperature to drive off surface bound water and hydroxide ions, subsequent irradiation produced a decreased amount of ionized products of the adsorbed aromatic compounds suggesting the necessity of chemisorbed water on the oxide surface.[5] Holes, on the other hand, get trapped or react with H atoms and surface bound hydroxyl groups to form surface bound protons and hydroxyl radicals, respectively. On the basis of the information above and on HCB reaction on alumina,[3] a mechanism of surface promoted degradation of an adsorbed contaminant is proposed in Scheme 1.

The degradation process in Scheme 1 is affected by the presence of surface adsorbed oxygen and excess water. Because oxygen is a good electron scavenger,[23,24] it competes with HCB for the conduction band electrons. The retarding effect of these surface adsorbed species can be overcome by carrying out the irradiation under vacuum. These observations further ascertain the domination of a reductive process in the dechlorination of HCB.

The presence of moisture on the surfaces of silica and alumina clearly had profound effects on the degradation of HCB. Past work has found that surface adsorbed moisture on titania led to enhanced electron/hole recombination.[25] Given the extreme hydrophobicity of HCB, we may expect a certain degree of HCB displacement from oxide surfaces by water molecules, breaking the monolayer arrangement of HCB and thus, decreasing the HCB/surface interactions. Indeed, water addition to silica and alumina has been shown, by NMR studies, to result in an

TABLE 2: *G* Values ($\times 10^{-3}$) of Dechlorinated Products Following 4-Hour Irradiation (58.2 kGy)[a]

experimental condition	product	alumina	σ_{Al}	silica	σ_{Si}	zirconia	σ_{Zr}	zeolite	σ_{Zeo}
water sat	PeCB	2.0	0.06	5.3	0.16	0.58	0.018	1.8	0.055
open atmosphere	PeCB	8.8	0.27	20.0	0.63	1.8	.056	2.6	0.081
vacuum	PeCB	176.0	5.5	110.9	3.4	9.4	0.29	15.0	0.46
vacuum	TeCB	6.0	0.2	4.0	0.13	0.21	0.0065	0.62	0.020

[a] Standard deviation (σ) values for average *G* values are presented. Furthermore, titania/HCB samples irradiated in open atmosphere have a very low *G* value of conversion (2.6×10^{-4}).

SCHEME 1: Radiation Induced Processes in Large Band-Gap Oxides

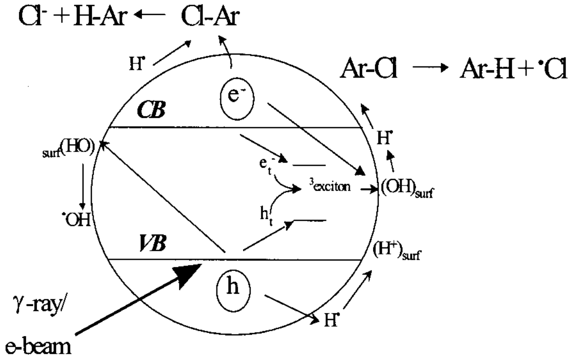


TABLE 3: Band Edge Properties of Metal Oxides

metal oxide	band-gap [eV]	E_{VB} [V vs NHE]	E_{CB} [V vs NHE]
Al_2O_3	8.45−9.9[a,b]	4.09[b]	−4.21[b]
SiO_2	8−8.9[a,b,c,f]	4.26[f]	−4.24[f]
TiO_2	3.0−3.3[a,d]	2.97[d]	−0.17[d]
ZrO_2	5.0[e]	4.0[e]	−1.0[e]

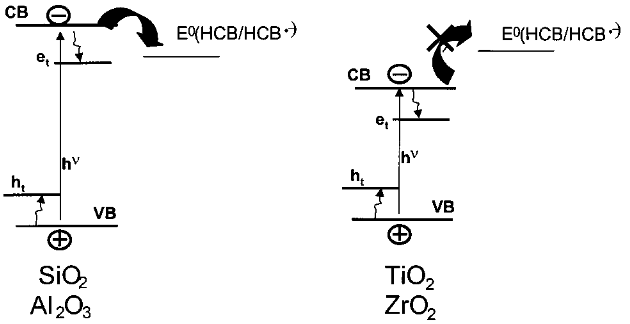
[a] Ref 33. [b] Ref 2. [c] Ref 34. [d] Ref 35. [e] Ref 36. [f] Ref 37.

increase in the mobility of benzenoid compounds when adsorbed to these surfaces.[26−28] Water adsorption leads to the blocking of strong adsorption sites, otherwise available for the adsorption of organics.[26] The results shown in Figures 3−5 suggest that the displacement of HCB by water to be greater on alumina than on silica.

The water adsorption capacity of metal oxides is influenced by such factors as dehydration conditions, pore size distribution, and surface area.[29] Because the adsorption of aromatic compounds such as HCB to the surfaces of alumina and silica occurs via physisorption,[26,28] the surface interactions are readily affected by water adsorption. Past research with chlorinated benzene compounds in alumina and silica solutions showed a greater degree of adsorption of these chemicals on silica than alumina.[30−32] In fact, the disparity in organic adsorption to alumina and silica increased upon chlorine substitution, a result of increased dipole interactions between the aromatic ring and the surface of the metal oxides.[30] These adsorption experiments are consistent with the results in the present research, which demonstrate decreased HCB degradation, presumably due to decreased adsorption, on the surface of alumina in the presence of water.

An important observation in the present study is our demonstration that the HCB degradation on metal oxides is dependent upon the energetics of the conduction band of the metal oxide, especially in evacuated samples. Information concerning the electronic properties (Table 3) of metal oxides provides further credence to our argument that the oxides are capable of catalyzing the radiation induced transformation of adsorbed substrates.

SCHEME 2: Band Edge Positions for Metal Oxides



The band-gaps of both alumina and silica are larger than those for titania and zirconia. The incident gamma rays are sufficiently energetic enough to induce charge separation in all these oxide materials. However, the difference from the reducing property is evident from the difference in the conduction band energy levels of these oxides. In contrast to TiO_2 and ZrO_2, the conduction band energies of alumina and silica are highly negative (∼−4.2 V vs NHE). Because the reduction potential of HCB is −1.2 V vs NHE,[38] only silica and alumina substrates are capable of reducing HCB effectively. Indeed, this relationship between the reduction potential of HCB and the conduction band energies of the metal oxides is consistent with our observation of higher yields of dechlorinated products in irradiated alumina and silica samples. The titania and zirconia remained ineffective catalysts to induce transformations of HCB. The energy levels of oxides and the reduction potential of HCB that illustrate the two different scenarios are summarized in Scheme 2.

Zeolites are Si−Al−O oxides which, upon irradiation, would also lead to the production of trapped holes and electrons.[4,39] These trapped holes are stabilized within the zeolite or react with surface absorbed organics. Low reactivity of zeolite in inducing reductive dechlorination shows that the electrons and holes that are produced during gamma irradiation undergo quick recombination or the electrons are scavenged by impurities or traps present in the zeolite framework. Trapping of electrons has also been shown to lead to color centers in zeolites,[40] a phenomena witnessed in our zeolite samples. As shown earlier, the cation clusters play an important role in the stabilization of electrons in dehydrated zeolites.[39,41] The competition between cation stabilization and electron hydration agrees with the decrease in HCB degradation on zeolites under a water-saturated atmosphere compared to samples under an open atmosphere.

Surprisingly, oxidative processes were not discovered on any of the oxide supports employed in the present investigation. Extractions of the irradiated oxide/HCB samples using polar/nonpolar solvent mixtures were conducted to probe for the formation of HCB oxidation byproducts such as phenol, chlorophenol, dichlorobenzoquinones, and dichlorohydroquinones. However, GC-ECD and GC-MS analysis of the samples irradiated for extended time periods (4 h) did not indicate even trace levels of oxidation products. Even the extended extraction procedures (solvent mixtures with varying polarity, sonication, and thermal desorption) did not yield any oxidation products.

Although it is surprising to see no direct evidence for a radiation induced oxidation process on oxide surfaces, such a phenomenon is not unprecedented. Schatz et al.[37] reported that the absorption of high-energy electrons by silica suspensions, led to electron ejection from silica as secondary electrons. They could observe only the reduction process at the solid/water interface and not the oxidative process. The absence of interfacial charge-transfer involving holes at the solid/water interface was indicative of the fact that the holes get trapped within the silica particle.

Conclusions

The results described in this study show the ability of oxides to act as catalysts in the radiolytic degradation of organic compounds. Only reductive pathways involving dechlorination of HCB occurred on oxide surfaces. The degradation yield is directly influenced by the intrinsic properties of the oxides. Alumina and silica with conduction band energy more negative than the reduction potential of HCB were most effective in inducing the reductive dechlorination. The present study highlights the merits of radiolysis in treating recalcitrant contaminants such as chlorinated benzene using metal oxides as catalysts. After the completion of the dechlorination step, one can consider a bioremediation or an advanced oxidation process to achieve complete mineralization. The radiation-induced catalysis may thus be useful as a pretreatment process for contaminated soils.

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Supporting Information Available: FTIR spectra obtained for all 5 HCB coated oxide samples before and after irradiation under an open atmosphere. This material is available free of charge via the Internet at http://pubs.acs.org.

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