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Halide acid pretreatments of photocatalysts for oxidation of aromatic air contaminants: rate enhancement, rate inhibition, and a thermodynamic rationale

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Abstract

The effects of chlorine radical generation during the photocatalytic oxidation of aromatic contaminants in air can be significant. Previous studies have shown that cofeeding chlorinated olefins (TCE, PCE) may increase the removal of branched aromatics (toluene, xylenes), presumably by initiating chlorine radical chain reactions. Hydrochloric acid catalyst pretreatments produce a similar enhancement of aromatic conversions. However, both approaches were ineffective for rate enhancement toward benzene, while hydrobromic and hydriodic acid pretreatments diminished the photocatalytic oxidation of both benzene and toluene. The present study broadens this halide acid inquiry to include hydrofluoric acid catalyst pretreatments and to examine halide acid influences on the removal of *m*-xylene as well. Only HCl pretreatments enhanced activity, and only for the branched aromatics (toluene and *m*-xylene). These results appear consistent with a thermodynamic analysis proposed here, which indicates that (1) fluorine radical generation is not energetically feasible under the conditions considered, (2) bromine and iodine radical generation is energetically feasible, but the radicals are insufficiently reactive to initiate the degradation of aromatics, and (3) chlorine radicals are predicted to be sufficiently energetic to abstract hydrogen from the methyl groups of branched aromatics, but not from the more strongly bound hydrogen atoms on the aromatic ring. These calculations are all in accord with our experimental results for the photocatalytic oxidation aromatics. The consistency of these thermodynamic arguments is also further support for the presumed halide radical pathway for rate enhancement.

Keywords: Photocatalysis; Photocatalyst; TiO_2; Aromatics; Benzene; Toluene; Xylene; Rate enhancement; Pretreatment; Chlorine; Halides; Radicals

1. Introduction

Photocatalytic oxidation in air of trace levels of benzene [1–3], toluene [4–6], and xylene [7,8] over titanium dioxide photocatalysts has been examined by several researchers. Although photocatalytic oxidation has proven effective, continuous-flow photocatalytic reactors for gas-phase aromatics generally yield only moderate conversions, and apparent catalyst deactivation is common. As a result, techniques are needed to increase the conversion of aromatic contaminants.

One technique involves the introduction of a second, more reactive contaminant into the gas stream. Berman and Dong [9] first demonstrated that cofeeding of a reactive, chlorinated compound like TCE in a gas stream can significantly increase the decomposition rate of certain organic contaminants, including isooctane, methylene chloride, and chloroform. Several additional studies further examined the effects of cofed TCE on the photocatalytic oxidation of a variety of organic contaminants [10–13].

Luo and Ollis [11] demonstrated that this technique could be used to increase the conversion of an aromatic, toluene, in the gas phase: near-complete photocatalytic oxidation of toluene at 88.5 mg/m^3 in the presence of TCE (753 mg/m^3) was demonstrated. Based upon homogeneous gas-phase TCE degradation pathways described by Sanhueza et al. [14] and the chlorine radical pathway adopted by Nimlos et al. [15] for photocatalyzed TCE oxidation, Luo and Ollis proposed a chain-transfer reaction mechanism, in which surface chlorine radicals generated by TCE degradation could react with a second adsorbed reactant (toluene) via

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hydrogen abstraction, thereby initiating toluene oxidation and increasing both removal rate and overall conversion.

A further report by Sauer et al. [16] demonstrated that two other chlorinated olefins, perchloroethylene (PCE) and trichloropropene (TCP), could be cofed and used to enhance the photocatalytic degradation of toluene in a manner similar to that seen with TCE addition. d'Hennezel and Ollis [12] explored the effects of TCE addition on a range of aromatic compounds, including benzene, toluene, ethylbenzene, and *m*-xylene. The addition of TCE to the gas phase significantly increased the conversion of all three branched aromatic compounds, but had virtually no impact on benzene destruction.

Since introduction of an additional hazardous pollutant such as TCE into an airstream already contaminated with an aromatic compound is generally unappealing as a process concept, an alternate approach was required to utilize the chlorine promotion effect. d'Hennezel and Ollis [17] examined the pretreatment of titania catalysts with hydrochloric acid solutions. Based upon previous studies by Primet et al. [18], Boonstra and Mutsaers [19], and Shastri et al. [20], d'Hennezel and Ollis proposed that these pretreatments introduced chloride anion groups into the titania surface structure. Under photocatalytic conditions, these chloride groups could be converted, via photogenerated hole (h^+) attack, into chlorine radicals, which could then react with adsorbed hydrocarbon species (e.g., via hydrogen abstraction), potentially producing rate enhancements. Photocatalytic oxidation experiments using these HCl-pretreated catalysts produced enhanced toluene conversion levels similar to results seen when TCE was cofed in the gas stream. When HCl-pretreated catalysts were used in the photocatalytic oxidation of benzene, however, conversion levels were reduced compared to those achieved with untreated catalyst samples [21]. This lack of enhancement was attributed to the relative stability of benzene toward chlorine radical attacks compared to other branched aromatic contaminants like toluene.

Lewandowski and Ollis [22] explored photocatalyst pretreatment with different acids, including hydrobromic acid (HBr) and hydriodic acid (HI), on the photocatalytic oxidation of toluene. Both HBr- and HI-pretreated catalysts displayed significantly lower activity than untreated titania catalysts, particularly during the initial period of reaction. We suggested that bromine and iodine radicals, if generated, might not be sufficiently energetic to react with toluene, but no specific supporting evidence was offered.

Minero et al. [23,24] examined the influence of fluoride-treated catalysts on the photocatalytic oxidation of phenol in aqueous media. Although the fluoride-treated titania was observed to increase the removal of phenol from solution, the enhancement was not derived from the generation of fluorine radicals. The high redox potential for the conversion of fluoride anions to fluorine radicals (3.6 V) makes surface fluoride anions stable against oxidation by photogenerated holes [23]. The enhancement in phenol oxidation was instead attributed to a shift in the form of reactive species generated by the photocatalyst under illumination. Minero et al. suggest that on untreated titania, reaction takes place through a combination of surface-bound radicals and direct electron transfer. Reactions involving solution-mobile reactive species are negligible under these conditions. On the fluoride-treated catalysts, however, the reaction mechanism shifts substantially toward reactive species mobile in the aqueous solution. The mobility of the radicals in solution allowed for enhanced oxidation of phenol, which binds only weakly to the catalyst surface. However, in our gas-phase photocatalytic oxidation, only surface reactions are expected to occur at ambient temperatures, so the potential impact of surface fluoride as a possible rate promoter under our conditions was unclear.

In the present gas–solid study, the effects of halide acid pretreatments on titanium dioxide catalysts have been reconsidered. Catalyst samples pretreated with hydrofluoric (HF), hydrochloric (HCl), hydrobromic, or hydriodic acid have been prepared and evaluated for use in the photocatalytic oxidation of gas-phase benzene, toluene, and *m*-xylene. The results of these experiments have been compared to thermodynamic calculations examining the ability of the photocatalyst to generate halide radicals and the energetics of such radicals in reactions with branched and unbranched aromatic compounds.

2. Experimental

2.1. Photocatalyst preparation

The catalyst pretreatment method employed was described previously [22] and is based upon the technique used by d'Hennezel and Ollis [17]. One gram of titanium dioxide powder (Degussa P25) is treated with 3 mL of an aqueous pretreatment solution, producing a thick slurry. Five different solutions are employed for the current series of experiments. The first, used as a control, consists of pure deionized water. The remaining four are 0.3 M solutions of either hydrofluoric acid, hydrochloric acid, hydrobromic acid, or hydriodic acid. The resulting slurries are permitted to stand for 5 min before being transferred to individual vacuum desiccators. The catalyst samples are allowed to dry under vacuum for up to 5 days. The extent of drying is monitored by weighing the samples once per day to estimate the quantity of water and acid removed. Once the drying is completed, the catalyst samples are ground using a mortar and pestle to break up agglomerates and to prepare the titania for use in photocatalytic experiments.

2.2. Gas-phase photocatalysis

Photocatalytic experiments are conducted using a single pass, continuous flow, powder layer photoreactor, described previously [7]. The system is prepared for use by first loading the pollutant reservoir with the compound of interest.

The required quantity of liquid benzene (Fisher, ACS grade), toluene (Fisher, HPLC grade), or *m*-xylene (Aldrich) is injected into the vapor feed reservoir, along with deionized water to provide the desired level of humidification. The reservoir is then sealed, gently heated until the pollutant and water have vaporized, and finally pressurized with scientific grade air to 15 psig. The gas stream from the pollutant tank is mixed with an additional stream of scientific-grade air to provide a steady feed for the duration of the photocatalytic run. In the current series of experiments, pollutant concentrations are set at 50 $\mathrm{mg/m^3}$, with water vapor concentrations of 1000 $\mathrm{mg/m^3}$.

The reactor vessel contains a 2-cm-diameter glass frit to support the photocatalyst of interest. One hundred milligrams of catalyst powder, either untreated Degussa P25 or one of the pretreated samples described above, is loaded into the reactor vessel. The powder is spread in a thin layer (approximately 1 mm thick) over the glass frit.

Before exposure to the pollutant of interest, the photocatalyst sample is briefly cleaned by simultaneous exposure to UV and flowing air for 45 min. Illumination is provided by a 100 W blacklight (Blak Ray B-100 A) placed above the reactor vessel. Once this cleaning step is completed, the catalyst is exposed to 60 $\mathrm{cm^3/min}$ of the contaminated airstream in the absence of illumination to allow for preadsorption of the contaminant of interest. Once dark-adsorption equilibrium has been reached, photocatalysis is started by unmasking the UV light source and restoring UV illumination.

A flame ionization detector (Perkin-Elmer Sigma 1) continuously monitors the reactor off-gas throughout the experiment. Previous experiments conducted with aromatic contaminants under these conditions did not reveal detectable levels of partial oxidation intermediates with GC/FID analysis; only unreacted aromatics were detected [11,12,16,21]. Under these conditions, the FID signal may be considered to provide a direct measure of the quantity of unreacted contaminant remaining in the reactor off gas.

3. Experimental results

3.1. Control experiments (untreated and water-pretreated titania)

Photocatalytic oxidation reactions for each of the three pollutants considered were carried out on untreated titanium dioxide powders as a base case for comparison with treated catalyst samples. In each case, the pollutant concentration in the reactor off gas is observed to drop from the maximum level (50 $\mathrm{mg/m^3}$) just before the start of illumination to a minimum after just a few minutes of UV exposure. The initial level of removal varied depending upon the contaminant, with benzene showing the least removal (40–45%) (Fig. 1). Toluene and *m*-xylene both show initial removal levels of 85% or more.

As the photocatalytic reaction continues, pollutant conversions begin to decrease. A relatively gradual decrease is observed for benzene, while a more rapid decrease is seen with toluene and *m*-xylene. The pollutant concentration in the exit stream appears to approach a pseudo steady-state level with all three compounds, although the time required to reach this state varies from approximately 1 h for benzene to 2.5 h for toluene and more than 6 h for *m*-xylene.

Photocatalysis experiments were also conducted using catalyst samples that had been pretreated with deionized water and dried using vacuum desiccation. Catalyst samples treated in this way have been used previously as controls to examine the effects of the aqueous treatment process and vacuum desiccation on the titania catalyst material [17,21,22]. As in these previous studies, the water pretreatments are observed to have relatively little effect on the behavior of the catalyst (Fig. 1).

3.2. HCl-pretreated titania

The use of an HCl-pretreated catalyst has a different influence for each of the three contaminants tested. Benzene

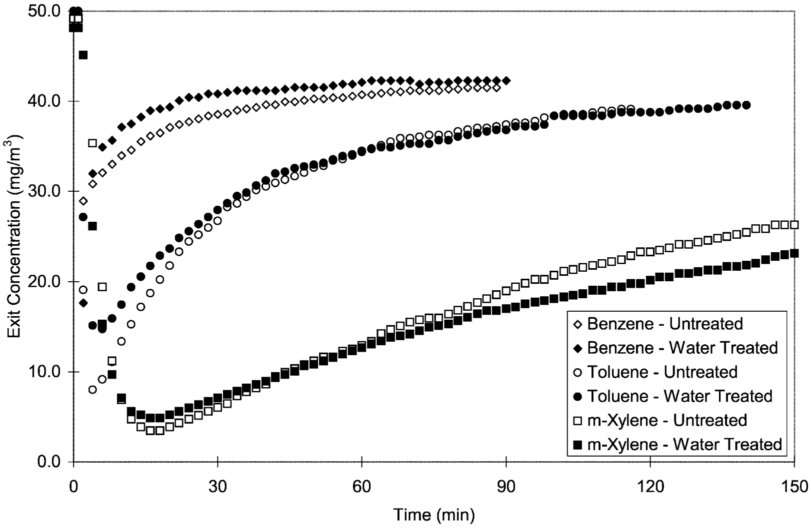

Fig. 1. Photocatalytic oxidation of benzene, toluene, or *m*-xylene (50 $\mathrm{mg/m^3}$) on untreated titania and water-pretreated titania.

removal is observed to be significantly lower on HCl-pretreated catalysts compared to either untreated and water-pretreated samples (Fig. 2). The initial removal maximum seen with untreated catalysts is absent on the HCl-pretreated sample, and the apparent steady-state removal is reduced by nearly a third.

Toluene removal is initially increased when HCl-pretreated titania is used (Fig. 3), as previously reported [17]. Peak toluene removal is increased slightly, and the level of removal exceeds that seen using untreated or water-pretreated catalysts for several hours. The use of HCl-pretreated catalysts is found here to not affect the level of removal observed at steady-state, however, suggesting only a transient promotion from the HCl pretreatment.

Xylene removal does not appear to be substantially affected by the use of the HCl-pretreated catalyst (Fig. 4). Initially, the removal of m-xylene is observed to increase modestly, and at longer times (beyond 1 h) it is slightly hindered on the HCl-pretreated catalyst material. In both cases, the effect is relatively minor compared to what is seen with benzene and toluene.

3.3. HF-pretreated titania

Titania samples pretreated with HF solution produce no increase in activity for any of the contaminants considered. Photocatalytic oxidation of toluene appears to be nearly unaffected by the HF pretreatment (Fig. 3), while benzene and m-xylene both show decreased levels of removal (Figs. 2 and 4).

3.4. HBr- and HI-pretreated titania

Both HBr- and HI-pretreated catalysts exhibit significantly reduced catalyst activity for all three contaminants

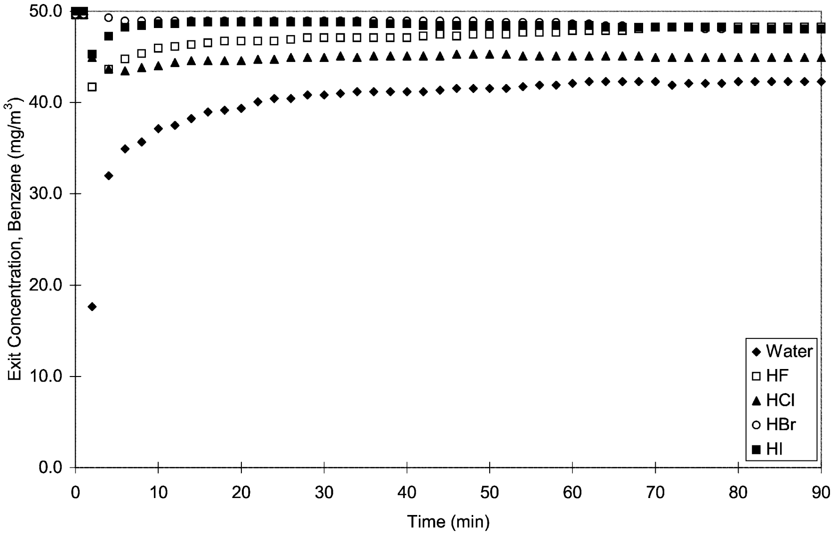

Fig. 2. Photocatalytic oxidation of benzene (50 mg/m^3) on halide acid-pretreated titania.

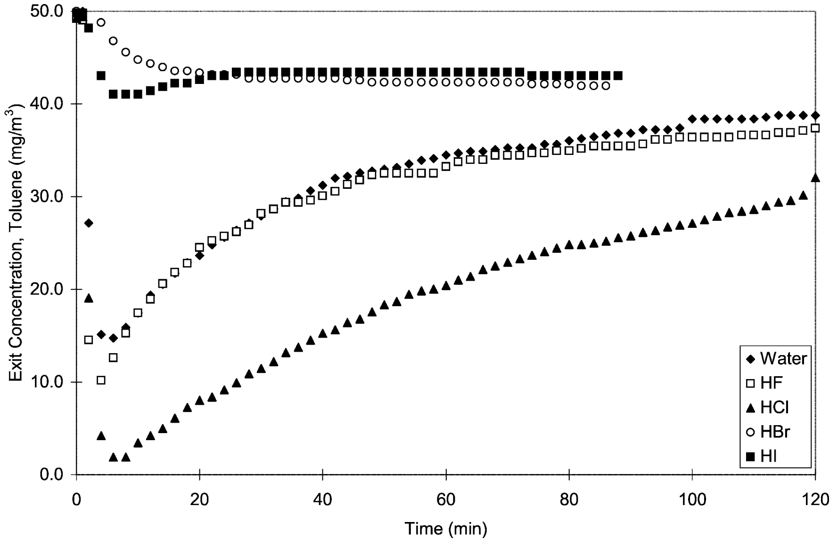

Fig. 3. Photocatalytic oxidation of toluene (50 mg/m^3) on halide acid-pretreated titania.

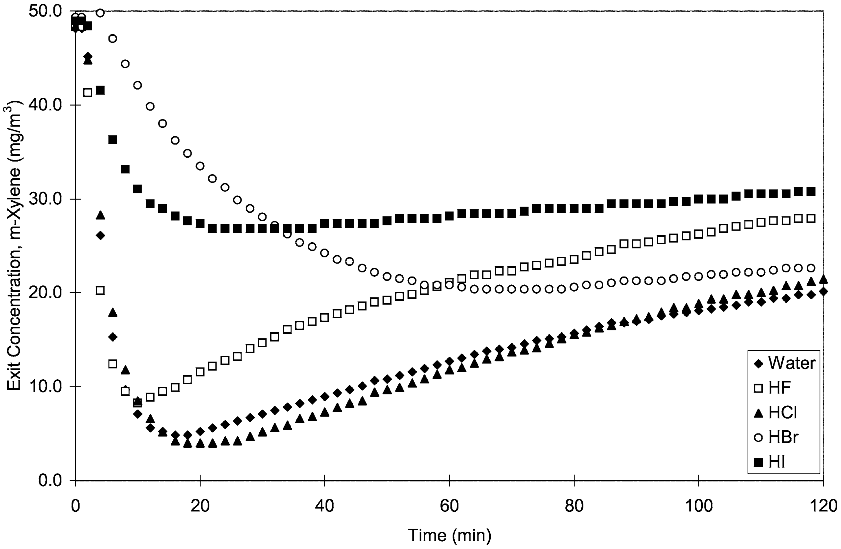

Fig. 4. Photocatalytic oxidation of m-xylene (50 mg/m^3) on halide acid-pretreated titania.

(Figs. 2–4), and the period of maximum removal is either significantly reduced in duration or completely eliminated. The effect is most pronounced with toluene, where the peak removal of the contaminant is reduced from roughly 80% on untreated catalysts to approximately 20% with HBr- or HI-pretreated catalysts. The reduction in the removal level is nearly as severe for benzene, although the lower initial removal levels seen with benzene make the effect less pronounced. The inhibitory effects of the HBr and HI pretreatments are not as severe for m-xylene, but the reductions are still significant.

Steady-state removal levels appear to be unaffected by the HBr and HI pretreatments in both the toluene and m-xylene systems. With benzene, however, the HBr and HI pretreatments appear to produce a reduction in the steady-state removal level, from approximately 16–18% to only 4–5%.

4. Discussion

4.1. Radical generation

As described previously, several studies involving chlorinated organics have proposed that chlorine radicals may be generated during photocatalysis [15], and these radicals may then participate in radical chain reactions with other adsorbed compounds, including branched aromatics [11,12,16]. Recent studies proposed that pretreatment of the titania catalyst with HCl may also facilitate the formation of chlorine radicals during photocatalysis, leading to enhanced conversion of certain contaminants which are susceptible to chlorine radical attack [17]. We have also suggested that titania catalysts pretreated with the halide acids HBr and HI may lead to radical generation as well [22].

d'Hennezel and Ollis proposed a mechanism for chlorine radical generation in which HCl pretreatment leads to a substitution of chloride groups for hydroxyl groups on the catalyst surface during the pretreatment process [17]. Under UV illumination, these chloride groups could be converted to chlorine radicals by photogenerated holes. XPS analysis of fresh catalyst samples indicated that chlorine was present on the catalyst surface prior to use and was most likely in the form of chloride. XPS experiments carried out as part of this study also detected chlorine on titania pretreated with HCl solutions, as well as detecting bromine on samples pretreated with HBr and iodine on samples pretreated with HI. The XPS experiments revealed an initial atomic ratio of approximately 27.8 chlorine atoms per 100 titanium, which is consistent with the previous results reported by d'Hennezel and Ollis [17]. The estimated atomic ratio of bromine to titanium was somewhat lower (8.1 bromine atoms per 100 titanium atoms), and the iodine to titanium ratio was lower still (3.2 per 100 titanium atoms). This trend may be due to steric influences or the increasingly diffuse charge of the larger halide anions, which may lead to reduced ion exchange during the pretreatment process.

We note here an alternate pathway which may also contribute to chlorine radical generation via direct photolysis of adsorbed HCl molecules. Direct photolysis would only occur during UV illumination of the catalyst, but would not require prior dissociation of the HCl molecule or electron/hole generation by the photocatalyst in order to operate. A photolysis reaction could occur in parallel with conventional photocatalytic reaction pathways, adding a supply of chlorine radicals to the reactive species normally formed during TiO_2 photocatalysis. Although the H–Cl bond energy (431.62 kJ/mol [30]) would normally be greater than the energy provided by UV radiation of the wavelengths typically employed in photocatalytic studies (300–400 nm, which provides 398.8 to 299.1 kJ/mol), binding with the catalyst surface may weaken the H–Cl bond sufficiently to allow for photolysis at the wavelengths of interest. Some of the HCl bound in this manner may not, however, be bound strongly enough to remain on the catalyst surface under the ultra-high vacuum conditions required for XPS analysis. As a result, XPS data on halide populations resulting from acid pretreatment may underestimate the quantity of nondissociated acid available, particularly if direct photolysis is a significant pathway for radical formation.

4.2. Radical reaction thermodynamics

A number of different active species have been suggested to operate in photocatalytic systems, including hydroxyl radicals, holes (h^+) [25], and anion vacancies [26]. Most often, photocatalytically generated hydroxyl radicals are assumed to attack adsorbed contaminant molecules through a hydrogen abstraction reaction

$$\mathrm{OH}\cdot + \mathrm{R{-}H} \rightarrow \mathrm{HOH} + \mathrm{R}\cdot.$$

As an initial assumption here, halide radicals, regardless of their specific route of generation, may be considered to react in parallel with photogenerated hydroxyl radicals via similar pathways

$$\mathrm{X}\cdot + \mathrm{R{-}H} \rightarrow \mathrm{HX} + \mathrm{R}\cdot.$$

However, the reactivity of fluorine, chlorine, bromine, and iodine radicals toward hydrocarbons will vary, and the reactivity will differ from that for hydroxyl radicals. Further, for the case of branched aromatic contaminants, the bond energies of the methyl group hydrogens will be lower than those of ring hydrogens. To determine which reactions may be expected to occur spontaneously in the photocatalytic system, the thermodynamics of each radical (OH·, F·, Cl·, Br·, and I·) reacting with representative aromatics (benzene-ring hydrogen, toluene-branch hydrogen) must be considered.

Ideally, the variable to calculate is the free energy change of the reaction, ΔG_{rxn}. However, neither ΔG nor ΔS data for radical species are readily available in the literature. Enthalpy data (ΔH_{form}) are available, however, allowing for relatively straightforward calculation of enthalpies of reaction. Considering the relatively low temperatures at which the photocatalytic surface reaction operates, ΔH_{rxn} should provide a reasonable prediction of which reactions can be expected to proceed spontaneously.

Table 1 provides heat of formation data for gas-phase hydroxyl radicals and for the various halide radicals considered here, along with the standard states from which these radicals are generated [27]. Table 2 lists heat of formation data for products (acids) resulting from hydrogen abstractions [27]. Table 3 provides heat of formation data for benzene (C_6H_6) and toluene ($C_6H_5CH_3$) [28], along with corresponding organic radicals ($C_6H_5\cdot$ and $C_6H_5CH_2\cdot$, respectively) [29]. Using these heats of formation, corresponding heats of reaction, ΔH_{rxn}, for hydrogen abstraction reactions may be computed for each radical of interest reacting with either a benzene ring hydrogen (Table 4) or a toluene methyl hydrogen (Table 5).

Table 1
Heats of formation for pertinent radicals [27]

	OH·	F·	Cl·	Br·	I·
ΔH_{form} (kJ/mol)	38.95	78.99	121.68	111.88	106.84
Standard states	$\frac{1}{2}O_{2\,(g)} + \frac{1}{2}H_{2(g)}$	$\frac{1}{2}F_{2\,(g)}$	$\frac{1}{2}Cl_{2\,(g)}$	$\frac{1}{2}Br_{2\,(l)}$	$\frac{1}{2}I_{2\,(s)}$

Table 2
Heats of formation of acids [27]

	HOH	HF	HCl	HBr	HI
ΔH_{form} (kJ/mol)	−241.81	−271	−92.306	−36.4	26.5

Table 3
Heats of formation of benzene, toluene, benzene radical, and toluene radical [28,29]

	C_6H_6	$C_6H_5CH_3$	$C_6H_5\cdot$	$C_6H_5CH_2\cdot$
ΔH_{form} (kJ/mol)	82.925	49.998	329	200

Table 4
Calculated heats of reaction for hydrogen abstraction from benzene

	ΔH_{rxn} (kJ/mol)
$\mathrm{OH}\cdot + C_6H_6 \rightarrow \mathrm{HOH} + C_6H_5\cdot$	−34.84
$\mathrm{F}\cdot + C_6H_6 \rightarrow \mathrm{HF} + C_6H_5\cdot$	−104.18
$\mathrm{Cl}\cdot + C_6H_6 \rightarrow \mathrm{HCl} + C_6H_5\cdot$	31.95
$\mathrm{Br}\cdot + C_6H_6 \rightarrow \mathrm{HBr} + C_6H_5\cdot$	97.65
$\mathrm{I}\cdot + C_6H_6 \rightarrow \mathrm{HI} + C_6H_5\cdot$	165.58

Table 5
Calculated heats of reaction for hydrogen abstraction from toluene (methyl side group)

	ΔH_{rxn} (kJ/mol)
$\mathrm{OH}\cdot + C_6H_5CH_3 \rightarrow \mathrm{HOH} + C_6H_5CH_2\cdot$	−130.77
$\mathrm{F}\cdot + C_6H_5CH_3 \rightarrow \mathrm{HF} + C_6H_5CH_2\cdot$	−200.12
$\mathrm{Cl}\cdot + C_6H_5CH_3 \rightarrow \mathrm{HCl} + C_6H_5CH_2\cdot$	−63.99
$\mathrm{Br}\cdot + C_6H_5CH_3 \rightarrow \mathrm{HBr} + C_6H_5CH_2\cdot$	1.71
$\mathrm{I}\cdot + C_6H_5CH_3 \rightarrow \mathrm{HI} + C_6H_5CH_2\cdot$	69.64

As seen in Tables 4 and 5, hydrogen abstraction reactions involving photocatalytically generated hydroxyl radicals are thermodynamically feasible (ΔH_{rxn} is negative), for the removal of both methyl group hydrogen on toluene and aromatic ring hydrogen on benzene. Abstraction of methyl group hydrogen is also thermodynamically more favorable than abstraction of ring hydrogens. These thermodynamic predictions are consistent with our experimental results, in which both benzene and toluene are subject to photocatalytic degradation, but where benzene displays lower removal rates than toluene. The thermodynamic predictions for the action of halide radicals vary depending upon the halide type and are described below.

4.3. Fluorine radicals

Thermodynamic calculations indicate that fluorine radicals should be capable of attacking aromatic contaminants and that such reactions should be even more thermodynamically favorable than the reaction of photocatalytically generated hydroxyl radicals with aromatic contaminants (Tables 4 and 5). However, these calculations consider only the effects of previously formed fluorine radicals on aromatic contaminants; they neglect the energy input required to generate the radicals. The generation of fluorine radicals requires a considerable energy input, either through absorption of light by the TiO_2 catalyst or by absorption by adsorbed HF molecules.

The conversion of fluorine anion to fluorine radical may be expressed as a half-cell reaction of the form

$$F^-_{(aq)} \rightarrow F_{(g)} + e^-.$$

The half-cell potential, or the energy input required to drive this reaction, may be calculated from the Gibb's free energy of formation of the product minus the Gibb's free energy of formation of the reactant. For the conversion of fluorine ion to fluorine radical, the half-cell potential is calculated to be -3.53 eV, while the band gap energy of titanium dioxide is only 3.2 eV. Surface fluoride groups should therefore resist oxidation by holes (h^+) generated by the illumination of the titania photocatalyst, so fluorine radical generation is not expected via this pathway [23]. Similarly, the bond energy of molecular HF has been measured as 570.3 kJ/mol [30]. Illumination of a wavelength of approximately 210 nm or less would be required to provide sufficient energy to photolyze this bond, a wavelength far below the 300–400 nm UV illumination provided in the experimental system. Even if illumination of this energy were provided, direct photolysis and degradation of the aromatic would be expected to occur under such illumination, even in the absence of HF or the titania photocatalyst.

Thus, although fluorine radicals would appear, from a thermodynamic perspective, to be sufficient to initiate the photocatalytic oxidation of aromatic contaminants, the energy required to generate such radicals is not available in the photocatalytic experimental system. No increase in catalyst activity is observed on our titania catalysts pretreated with HF during the gas-phase photocatalysis of aromatics. Residual HF on the catalyst, or fluorine anion groups incorporated into the catalyst surface, may affect binding of the aromatic contaminants to the titania or hydroxyl radical generation, producing the decreased activity seen in the photocatalytic oxidation of benzene and *m*-xylene on HF-pretreated catalyst samples. However, it is not clear why benzene and *m*-xylene photooxidation is reduced, while toluene photooxidation appears to be virtually unaffected by HF pretreatment of the catalyst.

4.4. Chlorine radicals

Chlorine radicals are less energetic than fluorine radicals, and even hydroxyl radicals. This indicates that it should be possible for chlorine radicals to be formed under the conditions present in a photocatalytic system. Calculation of the heats of reaction of chlorine radicals with toluene branch hydrogens suggests that such a reaction should occur (Table 5). Reaction with benzene ring hydrogens, however, is not predicted to be thermodynamically favorable (Table 4). This suggests that the presence of chlorine radicals should not assist in the photocatalytic oxidation of benzene or other compounds of comparable stability, but should be capable of attacking the weaker bound branch hydrogens of toluene or *m*-xylene, potentially boosting initial reaction rates.

Experimentally, HCl pretreatments are found to have no positive influence on the photocatalytic oxidation of benzene. Benzene removal is slightly suppressed on HCl-pretreated catalysts, which may result from a loss of active sites or from an increase in hydroxyl radical termination reactions due to interactions with photogenerated chlorine radicals.

The removal of the branched aromatic toluene is initially increased over HCl-pretreated titania, suggesting that chlorine radical reactions are taking place. This effect appears to last for up to 2 h, until the photocatalytic reaction begins to stabilize at a pseudo-steady-state level. The use of HCl-pretreated material does not appear to influence the steady-state extent of removal. This may be due to depletion of chloride groups over time, since the pretreatment is essentially a batch process and provides only a limited number of chloride groups. However, the effect may also result in part from the accumulation of more stable organic intermediate species on the catalyst surface.

The decline in catalyst activity commonly seen with aromatic contaminants is generally attributed to the accumulation of strongly bound, recalcitrant, partially oxidized intermediates on the catalyst [31]. Temperature-programmed hydrogenation (TPH) experiments conducted by Blount and Falconer indicate that recalcitrant intermediates generated during the photocatalytic oxidation of aromatic contaminants retain a ring structure [32]. In addition, measurements of oxygen uptake made by Larson and Falconer suggest the incorporation of several oxygen atoms into each contaminant molecule during the initial stages of photooxidation [31]. The higher photocatalytic reaction rates of branched aromatics as compared to benzene, as well as the reaction enthalpy calculations used here, suggest that side groups enhance reactivity, and that some oxidation of side groups likely occurs.

Oxidation of toluene's methyl group to an aldehyde or carboxylic acid functionality would reduce or eliminate the hydrogen abstraction reaction pathway attributed to chlorine radicals, since only the abstraction of side-group hydrogen atoms is thermodynamically favorable. As the population of recalcitrant material on the catalyst surface increases, it becomes increasingly likely that the photogenerated chlorine radicals will be unable to engage in oxidation reactions, and the initial enhancement effect seen with fresh toluene would be expected to gradually disappear, regardless of the catalyst's ability to supply additional chlorine radicals. Further oxidation of the recalcitrant intermediates is still possible through the action of hydroxyl radicals, however, since hydroxyl radicals are expected to be capable of abstracting hydrogen atoms from aromatic ring structures.

The photocatalytic oxidation of m-xylene is predicted to benefit from the presence of chlorine radicals in a manner similar to that seen with toluene. Such enhancement was reported previously for mixed contaminant streams containing m-xylene (50 $\mathrm{mg/m^3}$) and TCE (290 $\mathrm{mg/m^3}$) [12]. However, our experimental data for the photocatalytic oxidation of m-xylene on HCl-pretreated titania show little or no increase in m-xylene removal. This effect may result from the high loading of m-xylene on the catalyst. Dark adsorption measurements conducted for m-xylene and toluene show that nearly four times more m-xylene is initially adsorbed onto titania than toluene under comparable conditions (3.1×10^{-6} mol m-xylene per gram of titania, versus 8.2×10^{-7} mol toluene per gram of titania at 50 $\mathrm{mg/m^3}$ feed gas concentration, 1000 $\mathrm{mg/m^3}$ water vapor concentration).

This higher organic loading may hinder the chain reactions which make chlorine radicals so useful in boosting photocatalytic oxidation reactions, possibly by hindering the readsorption of HCl formed following hydrogen abstractions occurring during photocatalysis. If the higher coverage of m-xylene hinders the readsorption of HCl onto the catalyst surface, or disrupts the conversion of adsorbed HCl into species suitable for chlorine radical generation (such as the surface-bound chloride anion described by d'Hennezel and Ollis [17]), the chlorine radical chain reaction may be effectively terminated. Transport of HCl out of the illuminated zone of the catalyst could ultimately lead to depletion the chlorine inventory on the catalyst.

Such a disruption of the chlorine radical chain reaction has been suggested previously by Luo and Ollis in the photocatalytic oxidation of mixed contaminants [11]. During the simultaneous photocatalytic oxidation of toluene (80–550 $\mathrm{mg/m^3}$) and TCE (226 or 753 $\mathrm{mg/m^3}$), an enhancement in the toluene oxidation rate was observed when toluene concentrations were kept low (< 200 $\mathrm{mg/m^3}$). This enhancement was attributed to chlorine radical chain reactions produced by the photocatalytic dechlorination of the TCE. However, when toluene concentrations were increased (to more than 100 $\mathrm{mg/m^3}$ for the lower TCE concentration and to about 160 $\mathrm{mg/m^3}$ for the higher TCE concentration, approximately a 1:3 ratio), toluene removal rates dropped off to levels typical of toluene photocatalytic oxidation without chlorine radical reaction assistance. This effect was attributed to a "quenching" of TCE chain oxidation due to higher levels of organic material on the catalyst, thereby eliminating the continuous supply of chlorine radicals from TCE oxidation. Similar results were reported by Sauer et al. [16] for cofed toluene and TCP.

This quenching effect may impose a significant limitation on the range of conditions under which HCl-pretreated catalysts may be useful. As demonstrated by Luo and Ollis [11] and by Sauer et al. [16], the TCE or TCP cofed into a mixed air contaminant system may be adjusted to compensate for higher aromatic concentrations by simultaneously increasing the concentration of the chlorinated contaminant. With HCl-pretreated catalysts, however, the quantity of chlorine present in the system cannot be similarly increased. Previous studies examining the effect of different HCl pretreatment concentrations (0.3 N, 3 N, and 12 N) showed essentially no difference in the magnitude of the enhancement generated during toluene photocatalytic oxidation [22]. This suggests that there is a limit, achieved under all three of these concentrations, to the quantity of chlorine that may be incorporated into pretreated titania catalysts. This limited surface chlorine concentration may restrict the range of contaminant concentrations over which enhanced conversion levels may be achieved via chlorine radical chain reactions.

4.5. Bromine and iodine radicals

Thermodynamic calculations predict that neither bromine radicals nor iodine radicals should spontaneously react with either adsorbed benzene or toluene (Tables 4 and 5). These predictions are consistent with our experimental data, which show decreased activity on both HBr- and HI-pretreated catalyst materials for benzene, toluene, or m-xylene photocatalytic oxidation. All three aromatic contaminants show significantly reduced removal rates in the presence of HBr- or HI-pretreated catalysts. Although bromine and iodine radicals are predicted to be ineffective in initiating the desired oxidation of aromatic contaminants, they may still be generated on the catalyst surface. The generation of these radicals may thus result in nonproductive absorption of UV photons that might otherwise have produced useful reactive species. Once formed, bromine and iodine radicals may participate in side reactions, such as radical-radical termination reactions with hydroxyls, organic radicals, or other active species, hindering the desired oxidation reactions. This interference would be expected to continue until the supply of bromide or iodide decreased on the catalyst surface, allowing hydroxyl radical reactions to take place unhindered.

5. Conclusions

Thermodynamic calculations for the reaction of fluorine, chlorine, bromine, and iodine radicals with benzene or toluene have been used to provide insight into the effectiveness of halide-acid pretreatments on titania for use in photocatalytic systems. The results of these calculations are compared to experimental data, and a strong agreement between calculations and experiment is observed. Calculations predict that hydroxyl radicals are capable of initiating the oxidation of branched aromatic contaminants through their side groups. Benzene and other aromatic contaminants may also be attacked by hydroxyl radicals through the aromatic ring structure, but this reaction is not as energetically favorable as a reaction with side groups. Fluorine radicals, if generated, are predicted to be reactive toward either aromatic reaction site. However, a brief analysis of the energy requirements for the formation of fluorine radicals suggests that no radicals should be formed on titania catalysts under near-UV (long-wave) illumination. Chlorine radicals are predicted to be effective in oxidizing aromatic side groups, but ineffective in reactions with the aromatic ring. This is demonstrated experimentally on HCl-pretreated catalysts with increased activity toward toluene, but decreased activity toward benzene. Bromine and iodine radicals are calculated to be ineffective in oxidizing either the aromatic ring or methyl side groups, and experimental data show significantly reduced photocatalytic effectiveness over either HBr- or HI-pretreated catalysts for all aromatic contaminants considered.

Of the halide acid catalyst pretreatments considered, only HCl pretreatment shows any activity enhancements under the present experimental conditions. This enhancement was only observed for branched aromatics and appears to be effective only under the lower aromatic loadings seen with toluene. The enhancement is only effective during the early stages of photocatalysis; the accumulation of recalcitrant intermediates on the catalyst surface and/or the depletion of chloride groups produces a decline in the effectiveness of the pretreatment over time, with virtually no observable enhancement remaining when pseudo-steady-state conditions were reached. Thus, if catalyst pretreatment via HCl were to be utilized for enhanced oxidation of branched aromatic contaminants, a periodic retreatment or regeneration would appear to be necessary.

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