Reductive Activation of Dioxygen for Degradation of Methyl *tert*-Butyl Ether by Bifunctional Aluminum

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Bifunctional aluminum is prepared by sulfating aluminum metal with sulfuric acid. The use of bifunctional aluminum to degrade methyl *tert*-butyl ether (MTBE) in the presence of dioxygen has been examined using batch systems. Primary degradation products were *tert*-butyl alcohol, *tert*-butyl formate, acetone, and methyl acetate. The initial rate of MTBE degradation exhibited pseudo-first-order behavior, and the half-life of reaction was less than 6 h. XPS analysis indicates the formation of sulfate at the surface of bifunctional aluminum. The concentration of surface sulfate varies linearly with increasing strength of the sulfuric acid used during bifunctional aluminum preparation. The rate of MTBE degradation is a function of the concentration of the surface sulfate. MTBE degradation rates increased by a factor of 2 as surface sulfate concentrations increased from 233 to 641 μmol/m^2. This relationship implies that sulfate at the surface of bifunctional aluminum acts as a reactive site.

Introduction

Methyl *tert*-butyl ether (MTBE) is a common gasoline oxygenate that has been used since 1979 to reduce the level of carbon monoxide and volatile organic compounds from the emissions of motor vehicles. Rapid increase in the use of MTBE started in the early 1990s following the Clean Air Act Amendments regarding gasoline reformulation, making MTBE the fourth-highest produced organic chemical in the United States in 1998 (*1*). However, due to leaking underground storage tanks and pipelines, the contamination of groundwater with MTBE has become a concern. Recent studies suggest that MTBE has emerged as the second most frequently detected contaminant (after chloroform) in groundwater in the United States (*2*). Because of the unpleasant taste and odor, the U.S. Environmental Protection Agency has issued a Drinking Water Advisory that recommends MTBE control levels in the range of 20–40 μg/L of water.

The development of new efficient technologies for removal of gasoline oxygenates in water is an area of growing interest. Reductive activation of dioxygen represents a novel treatment concept for gasoline oxygenates. This process converts dioxygen, the most abundant, inexpensive, and environmentally compatible oxidant, into reactive radical oxygen

species whereas most existing oxidative technologies require strong oxidants such as peroxide or ozone (*3–5*). The formation of radical oxygen species can generally be expressed as eq 1, where [O] represents a reactive reduced oxygen species (*6*).

$$O_2 + 2H^+ + 2e^- \rightarrow [O] + H_2O \qquad (1)$$

Reductive activation of dioxygen has been identified in biological systems where enzymes such as cytochrome P450 are involved in the constructive use of dioxygen (respiration and oxidative metabolism) (*7*). However, few artificial systems, e.g., porphyrins (*7–9*), polyoxometalate anions (*10*), and O$_2$/H$_2$ fuel cells (*11–13*), are able to mimic this redox process. Reduced oxygen species such as superoxide ion and peroxide are strongly electrophilic (*14*). They have been used in many reactions including the oxygenation of alkanes and aromatics to alcohols and phenols, respectively (*11*). They could also serve as strong oxidants for the controlled degradation of gasoline oxygenates.

In general, the electron density at oxygen atoms is high under reducing conditions, which cause a decrease in their electrophilicity toward oxidizable substrates. For example, dioxygen molecules readily reduce to water through a four-electron-transfer process (*14*). Therefore, to generate oxygen radicals through the reductive activation of dioxygen, it is necessary to have specific catalysts or redox mediators that are capable of stabilizing these species. In artificial systems, porphyrins are known as effective catalysts, but they persist for only minutes in aqueous environments (*15*). The lack of suitable catalysts or redox mediators causes difficulties for the application of this process to environmental remediation.

Bifunctional aluminum, prepared by sulfating zerovalent aluminum with sulfuric acid, has been found to simultaneously degrade MTBE and carbon tetrachloride (*16*). This dual functionality of decomposing oxidatively- and reductively-degradable contaminants has been attributed to the capability of bifunctional aluminum to activate dioxygen through a reductive activation process. The objectives of this study were to determine the active species at the bifunctional aluminum surface. The results of batch experiments on the rate and extent of MTBE oxidation are presented, and an electron-shuttling process rationalizing the function of sulfur species is proposed.

Experimental Section

Materials. MTBE, *tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), methyl acetate, and acetone at reagent grade or better (>99%) were purchased from Aldrich. H$_2$SO$_4$ and concentrated HCl were obtained from Fisher and J. T. Baker, respectively. Aluminum powder (+99%, ~20 μm) was purchased from Aldrich. Aluminum sulfate and potassium sulfate were obtained from J. T. Baker.

Preparation of Bifunctional Aluminum. Bifunctional aluminum was prepared in a fume hood under ambient temperature and pressure. Ten milliliters of concentrated HCl was slowly added to a 500-mL glass beaker containing 5.0 g of aluminum powder, and the suspension was mixed with a magnetic stirrer. Immediate fume evolution was observed. Ten milliliters of Milli-Q water was added quickly to dissipate heat. Next, 0.5 mL of 1.0 N H$_2$SO$_4$ was added to the suspension and it was mixed again for 30 s. Five milliliters of concentrated HCl was added to the suspension followed by the addition of 1.0 mL of 1.0 N H$_2$SO$_4$. After the suspension was stirred for 30 s, 5 mL of concentrated HCl was added again and then the suspension was quenched with 15 mL of

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Milli-Q water. Finally, the suspension was stirred for 20 min before bifunctional aluminum was harvested via vacuum filtration. Sulfation of aluminum was also carried out by using different concentrations of sulfuric acid including 3.6, 9.0, and 18.0 N and different sulfate sources such as aluminum sulfate and potassium sulfate. Bifunctional aluminum used in the experiments was sulfated by 1.0 N sulfuric acid unless indicated otherwise. Acidification of aluminum metal by HCl (nonsulfated aluminum) was also prepared by using the same procedures except H_2SO_4 was not added.

Batch Experiments. Batch experiments were carried out in 160-mL serum bottles (150 mL nominal volume) each containing ~1.0 g of bifunctional aluminum unless indicated otherwise. For each batch bottle, a predetermined volume of MTBE stock solution was spiked into a 50-mL aqueous solution to achieve the desired initial concentration. A typical range of MTBE concentrations was between 0.16 (14.2 mg/L) and 0.016 mM (1.4 mg/L). Batch bottles were mixed on a shaker (50 rpm) at room temperature (22 ± 1 °C). At selected time intervals, 3-mL solution aliquots were transferred with a gastight syringe to 15-mL glass vials that were then filled with Milli-Q water with no headspace and immediately capped with a Teflon-faced septum and aluminum crimp cap. Control tests without bifunctional aluminum were conducted with identical experimental conditions and initial concentrations of reactants. Analyses of organic mass in the controls indicated that the mass varied by less than 5% over the course of a typical experiment. Measurements of pH indicated that solution pH varied from 3.9 to 4.6 throughout the experiments.

Analytic Methods. Qualitative identification and quantitative analysis of MTBE and associated reaction products were conducted by headspace-GC/MS analysis. Samples contained in 15-mL glass vials were loaded into a Tekmar 7000 headspace autosampler. The transfer line from the Tekmar 7000 is connected directly to a Varian 3400 gas chromatograph coupled to a Varian Saturn II ion trap mass spectrometer. The transfer line temperature was set at 200 °C. The GC was equipped with a DB-624 column (30 m × 0.25 mm × 0.5 μm). The oven temperature was programmed as follows: hold at 35 °C for 2.5 min and ramp at 8 °C/min to 235 °C for 1 min. Injection and detector temperatures were set at 175 and 200 °C, respectively. Carrier gas was He at 1.34 mL/min and split flow at 14.7 mL/min. The mass spectra were recorded under electron impact (EI) ion mode by conducting scans in the range of 40−250 m/z with data collection every 0.75 s. The linear range of calibration curves was conducted between 1 and 1000 μg/L.

Redox potential and pH were measured with an Orion pH/mV meter equipped with a combination redox electrode and a combination pH electrode, respectively. The E_h readings are reported relative to the standard hydrogen electrode (SHE). Dissolved oxygen (DO) concentrations were determined by using high-range dissolved oxygen kits CHEMetrics kit K-7512 (indigo carmine reagent).

Solid-Phase Characterization. Characterization of bifunctional aluminum was conducted by using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), a sulfur coulometer, and a surface area/particle size analyzer. XRD measurements were performed using a X-ray diffractometer MiniFlex (Rigaku Co.) at 30 kV and 15 mA with a copper target tube radiation (Cu Kα1) producing X-rays with a wavelength of 1.540 56 Å. Chemical speciation at the metal surface was analyzed by PHI Quantum 2000 XPS using monochromatized Al Kα (1486.6 eV) excitation under UHV conditions (5 × 10^{-8} Torr). The structure of metal particles was determined with a JEOL (JSM-5300) SEM. Concentrations of total sulfur in solid samples were determined by using a sulfur coulometer (UIC Inc.). The UIC sulfur coulometer measured sulfur as SO_2 gas.
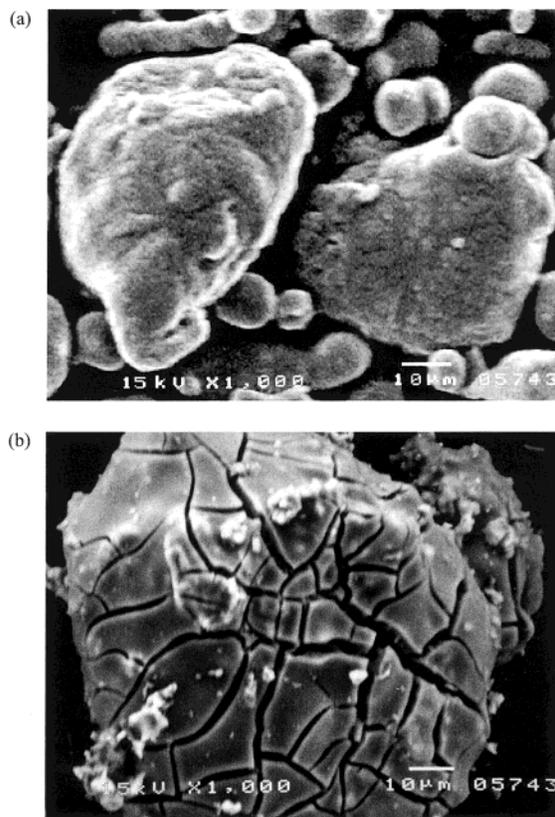
FIGURE 1. SEM micrographs of (a) untreated aluminum (1000×) and (b) bifunctional aluminum (1000×).

Samples were weighed into a ceramic boat, covered with vanadium pentoxide, and introduced to a combustion furnace set at 1050 °C. The BET surface area of aluminum particles was determined by using a Coulter SA 3100 surface area and pore size analyzer (Coulter Co.) using nitrogen (99.999% purity) as the analysis gas.

Results

Characterization of Bifunctional Aluminum. Figure 1 illustrates the SEM images of untreated aluminum powders and bifunctional aluminum. SEM studies show that bifunctional aluminum exhibited a cracklike structure, which was not found at the surface of untreated aluminum. This could be attributed to the aggressive etching of metal with strong acids during the preparation. The cracklike structure may increase the surface area through the formation of intraparticle spaces. The particle size distributions of untreated and bifunctional aluminum are shown in Figure 2. The untreated aluminum particles showed a single peak at ~20 μm while two peaks appeared in the size distribution curve of bifunctional aluminum. The major peak at 20 μm accounted for more than 70% (by volume) of the particles, while the minor peak at ~0.57 μm accounted for ~10% of the particles. This indicates that the sulfation resulted in the formation of small particles in the size range from 0.5 to 1.0 μm. The BET surface area of the bifunctional aluminum was 0.57 ± 0.03 m^2/g ($n = 3$), ~3 times greater than that of untreated aluminum powder (0.18 m^2/g, $n = 2$). The increase of surface area can be attributed to the reduction of particle size and the formation of intraparticle spaces.

Sulfur measurements indicate that the sulfation of aluminum resulted in the formation of sulfur-containing species at the metal surface. Approximately 0.54% (wt % S) was measured for the normally treated bifunctional aluminum whereas no sulfur was detected (<0.01 wt %) in
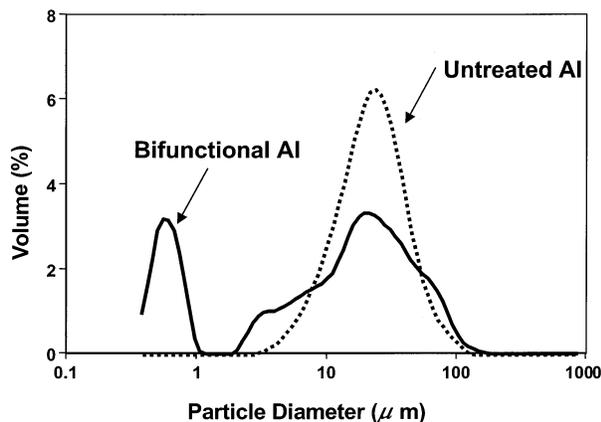
FIGURE 2. Particle size distributions of bifunctional and untreated aluminum.
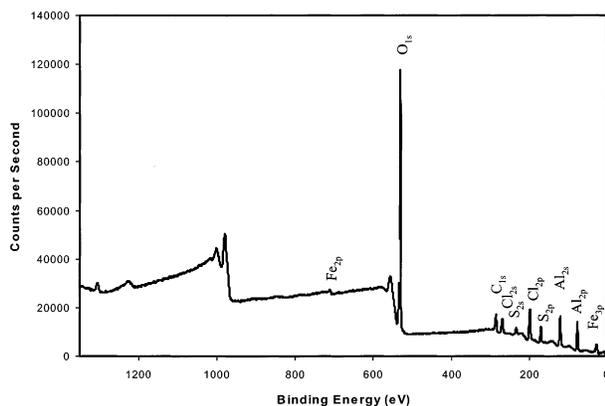
FIGURE 3. XPS spectrum of bifunctional aluminum.

TABLE 1. XPS Binding Energies (BE) of S and Al Species in Bifunctional Aluminum and Reference Samples

	BE (eV)	
sample	S_{2p}	Al_{2p}
SO_4^{2-}	169.1	
SO_3^{2-}	166.4	
S^0	163.6	
Al_2O_3		74.3
Al^0		72.9
bifunctional aluminum	169.4	74.8
C_{1s} (charge reference)	284.8	

nonsulfated aluminum. XRD and XPS analyses were conducted to further determine the speciation of sulfur. XRD results indicate only metallic aluminum; no sulfur-containing phases were detected. XPS, capable of probing 2−20 atomic layers, was used to obtain information on the elemental composition and the oxidation state of elements in the near-surface environment. An XPS spectrum of bifunctional aluminum prepared by sulfating aluminum metal with 18.0 N sulfuric acid is shown in Figure 3. The bifunctional aluminum was prepared under ambient conditions and sealed under nitrogen gas prior to analysis. Peaks due to Al, S, O, Cl, C, and Fe were readily assigned in accordance with binding energy tables (*17*). The presence of carbon is attributed to contamination by hydrocarbons (*18*). In addition, iron detected in trace amounts is likely due to contamination by impurities in the reagents used.

The measured binding energies of S and Al in bifunctional aluminum are listed in Table 1. The binding energies of reference samples including Al^0, Al_2O_3, S^0, SO_3^{2-}, and SO_4^{2-} obtained from the NIST database are also listed in Table 1
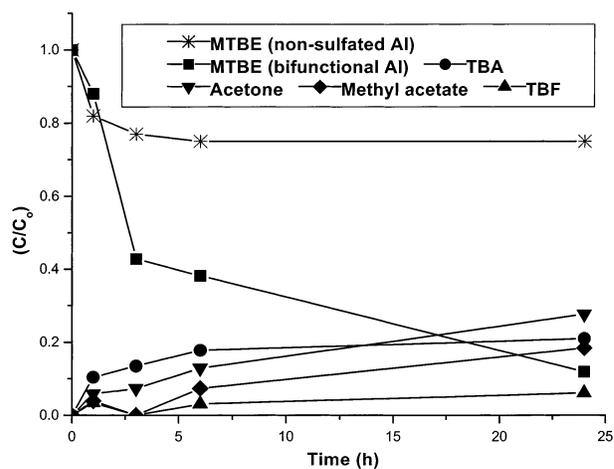
FIGURE 4. Transformation of 14.2 mg/L MTBE by bifunctional aluminum in the presence of dioxygen.

(*17*). Table 1 reveals that the 2p binding energy of S in bifunctional aluminum and that in a sulfate reference sample had values of 169.4 and 169.1 eV, respectively. This indicates that sulfate is the dominant form of sulfur at the surface of bifunctional aluminum. Furthermore, the 2p binding energy of Al at the bifunctional aluminum surface and that in aluminum oxide are 74.8 and 74.3 eV, respectively, indicating that the aluminum is present in an oxidized form, Al_2O_3, at the surface of bifunctional aluminum. Although aluminum oxide appeared at the metal surface, reduced aluminum (zerovalent aluminum) was still an abundant electron source underneath the oxide layer according to XRD analysis.

Transformation of MTBE. Typical results for the transformation of MTBE by bifunctional aluminum are shown in Figure 4. At an initial MTBE concentration of 14.4 mg/L, ~90% of MTBE was degraded by bifunctional aluminum within 24 h. Reaction products included acetone, methyl acetate, TBA, and TBF. Additionally, carbon disulfide was tentatively identified on the basis of GC/MS analysis. Acetone and methyl acetate accounted for about 27.6% and 18.4% of the MTBE lost, respectively. TBA increased continuously and remained steady throughout the experiment at a yield of ~21.0%. The yield of TBF was ~6.1% within 24 h. Furthermore, the MTBE removal efficiency after 24 h was improved to 99.5% when the initial MTBE concentration was 1.4 mg/L. Acetone, methyl acetate, and TBA accounted for 54.7%, 17.2%, and 13.2% of the MTBE lost, respectively. The overall carbon mass balance at the end of each experiment averaged ~85%. The remaining carbon (~15%) could be attributed to sorption of MTBE and its transformation products onto the metal surface, formation of carbon dioxide, or dissolved products not measured by GC.

The effect of the sulfation on aluminum was examined by using parallel experiments where nonsulfated aluminum was conducted to react with MTBE in the presence of dioxygen. Approximately 75% of initial MTBE still remained in the batch system within 24 h (Figure 4). No reaction intermediates such as TBF and TBA were found in the presence of nonsulfated aluminum. The E_h of the solution was −220 mV at the end of experiments. This test indicates that aluminum metal without sulfation cannot degrade MTBE. Furthermore, bifunctional aluminum prepared with different sulfate sources including K_2SO_4, and $Al_2(SO_4)_3$ showed similar effectiveness on MTBE degradation. It is clear that sulfation is an essential step for aluminum to degrade MTBE.

Trends in E_h and DO. The trend in E_h during MTBE batch experiments with bifunctional aluminum decreased from an initial value of +409 to −217 mV within the first 1 h and then increased slightly to −172 mV after a reaction period

of 24 h. The measured E_h values indicate that the batch systems were generally conducted under reducing conditions. Although the formation of aluminum oxide was found, it seems reasonable that a thin layer of aluminum oxide did not inhibit electron transfer at the metal surface. This is consistent with previous studies showing that the reductive dechlorination of carbon tetrachloride can occur in the presence of bifunctional aluminum (16).

Previous studies have demonstrated the effects of dioxygen on MTBE degradation by bifunctional aluminum (19). No measurable degradation of MTBE by bifunctional aluminum was found in the absence of dioxygen. Because the degradation of MTBE with bifunctional aluminum is an oxygen-dependent reaction, the removal of MTBE should involve the consumption of dissolved oxygen (DO).

$$C_5H_{12}O + O_2 \xrightarrow{\text{bifunctional aluminum}} C_5H_{10}O_2 + H_2O \quad (2)$$
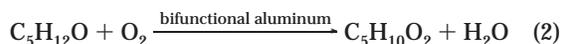
In this study, attempts were made to directly measure DO consumption in association with MTBE degradation. However, complete depletion of DO was observed when there were 22 mL of headspace in the 160-mL glass reaction bottle regardless of the presence or absence of MTBE. This indicates that aluminum metal reduces dioxygen and forms aluminum oxide.

$$4Al^0 + 3O_2 \rightarrow 2Al_2O_3 \quad (3)$$
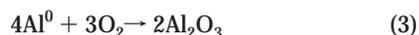
Approximately 191 μmol of headspace dioxygen was consumed by reaction with aluminum metal in a system with 22 mL of headspace within 24 h; however, less than 8 μmol of MTBE was degraded as indicated in Figure 4. This indicates that the reaction of dioxygen with aluminum metal is a major reaction in the bifunctional aluminum system. DO consumption attributed to MTBE oxidation accounted for only a small portion of the total DO consumption, which was largely due to dioxygen reduction by aluminum metal.

To capture the DO consumption rate from MTBE oxidation, experiments were designed to shorten the sampling interval from 24 to 6 h and to increase the initial MTBE concentration to 236.6 mg/L (54 μmol) in a 70-mL glass bottle. A measurable difference in the DO consumption rate was then found in a system with 50 mL of headspace. It was found that DO concentration was 3 mg/L in the aqueous solution in the absence of MTBE, while less than 1 mg/L DO was found in the presence of MTBE reacting with 1.0 g of 18 N bifunctional aluminum. This result provides direct evidence that the degradation of MTBE with bifunctional aluminum involves the consumption of dioxygen.

Rates of MTBE Degradation. The reaction kinetics of the transformation of MTBE was modeled with a pseudo-first-order rate equation

$$dC/dt = -k_{obs}C \quad (4)$$

where C is the concentration of MTBE in the aqueous phase (mg/L), k_{obs} is the observed first-order rate constant (h^{-1}), and t is time (h). Plots of the natural logarithm of MTBE concentration versus time through linear regression analysis gave straight line results. Linear regression analyses were used to obtain observed first-order rate constants. The disappearance of MTBE exhibited pseudo-first-order behavior. Typically, the coefficient of determination (r^2) was between 0.91 and 0.97. For example, best fits of the experimental data (Figure 4) to eq 4 indicated the observed rate constant was 0.11 h^{-1}, corresponding to a half-life of 6.3 h.

Discussion

MTBE is a chemically stable compound at ambient temperature and pressure. Although the direct oxidation of MTBE with oxygen is thermodynamically favorable, MTBE is
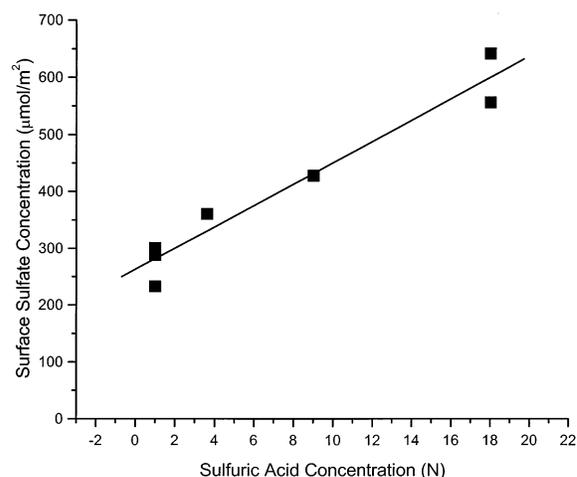
FIGURE 5. Effect of employed sulfuric acid concentrations on the formation of sulfate species at the bifunctional aluminum surface.

kinetically stable under ambient conditions. Consequently, MTBE is generally resistant to physicochemical degradation in natural environments. Studies have shown that the direct oxidation of oxygenates such as *tert*-amyl methyl ether by dioxygen occurs only at high temperature (20). Even in the presence of a strong oxidant such as ozone, the rate of the direct oxidation of MTBE is extremely slow (3). However, in the presence of bifunctional aluminum, degradation of MTBE with dioxygen occurs under ambient conditions. Evidence has shown that the formation of sulfur-containing species at the metal surface through sulfation plays a key role in MTBE degradation. The sulfation treatment may create active surface sites. XPS analysis further indicates that the sulfur-containing species are primarily in the form of sulfate. This suggests that the capability of bifunctional aluminum to degrade MTBE is attributed to the formation of sulfate at the aluminum surface.

Figure 5 illustrates the relationship between the sulfate concentration at the bifunctional aluminum surface and the concentration of sulfuric acid used during the sulfation process. The sulfur concentrations are expressed as specific concentrations of sulfate at the surface (μmol/m^2), which is obtained by normalizing total concentration by the specific surface area of bifunctional aluminum

$$SC \ (\mu mol/m^2) = (PC \ (\%) \times 10^4)/Ma_s \quad (5)$$

where SC is the specific concentration of sulfate at the surface (μmol/m^2), PC is the percentage concentration of sulfate (wt %), M is the molecular weight of sulfate, and a_s is the specific surface area (m^2/g). For example, sulfation of aluminum with 1.0 N sulfuric acid resulted in 0.54 wt % of sulfate precipitate at the metal surface, which is equivalent to 233 μmol/m^2. About 3 times more sulfate was found by using 18.0 N sulfuric acid. The effect of sulfuric acid concentration on the formation of surface sulfate is apparently linear, giving a least-squares regression line of

$$SC \ (\mu mol/m^2) = 18.727[H_2SO_4 \ concn \ (N)] + 262.96 \quad (6)$$

with a coefficient of determination of 0.945. Effects of surface sulfate concentrations on the rates of MTBE oxidation are shown in Figure 6. Increasing surface sulfate concentration from 233 to 641 μmol/m^2 increased rates of MTBE degradation by a factor of ~2. The relationship between the surface sulfate concentration and the reaction rates, k_{obs} (h^{-1}), appears to be linear, and regression of k_{obs} versus surface sulfate concentration gives

$$k_{obs} \ (h^{-1}) = 0.0001SC \ (\mu mol/m^2) + 0.0694 \quad (7)$$
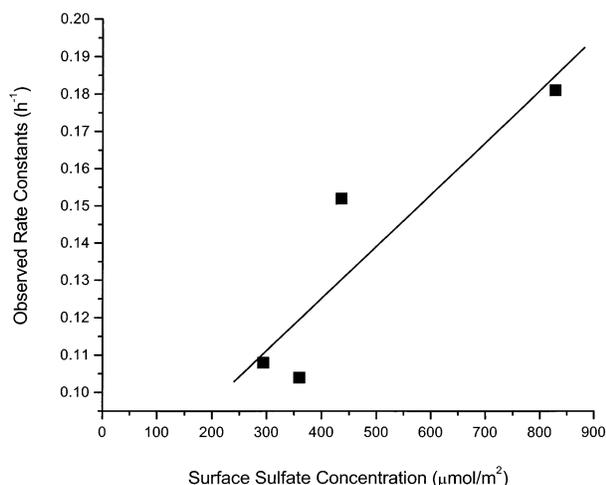
FIGURE 6. Effect of surface sulfate concentrations on the rates of MTBE degradation.
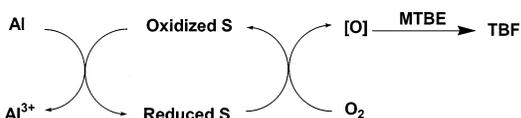
FIGURE 7. Conceptual model accounting for the roles of aluminum, surface sulfate species, dioxygen, and reduced oxygen species ([O]) in the oxidation of MTBE.

with a coefficient of determination of 0.82. This analysis indicates that the rate of MTBE oxidation by bifunctional aluminum is a function of sulfate concentration at the metal surface. This suggests that surface sulfate could act as a reactive center for stabilizing reduced oxygen species. However, the enhancement of MTBE oxidation is unlike a typical catalytic reaction where rates generally increase by at least 1 order of magnitude. Therefore, bifunctional aluminum is better recognized as a redox mediator.

The most common redox mediators involved in the reductive activation of dioxygen are transition metal–dioxygen complexes such as porphyrins (also known as catalysts). In general, transition metal species are (i) electron carriers that transfer electrons from electron sources to dioxygen through an electron-shuttling process and (ii) activators of dioxygen by reaction of transition metals with dioxygen to provide stable reduced oxygen species. For example, in the use of a photoexcited polyoxotungstate/iron porphyrin ($PW_{12}O_{40}^{3-}$/$Fe^{III}Por$) system for hydrocarbon oxidation, it has been suggested that the stabilization of reactive oxygen species is through redox coupling among $PW_{12}O_{40}^{3-}$/$PW_{12}O_{40}^{4-}$, $Fe^{III}Por/Fe^{II}Por$, and O_2/O_2^- (*8*). In the case of bifunctional aluminum, a postulated mechanism rationalizing the stabilization of the reductive oxygen species by sulfate during the reductive activation of dioxygen is illustrated in Figure 7. Sulfate acts as an electron carrier that transfers electrons from aluminum metal to dioxygen. Aluminum metal serves as the electron source for the reduction of oxidized sulfur species (sulfate), thus creating an active site (reduced sulfur) where dioxygen can be reductively activated. Although the identify of the reduced sulfur species involved in the electron-shuttling process remains uncertain, the formation of carbon disulfide indicated the existence of reduced sulfur species. The proposed electron-shuttling process accounts for the use of dioxygen to degrade MTBE despite the reduction of dioxygen to aluminum oxide that occurs simultaneously.

In this study, bifunctional aluminum has been demonstrated to be capable of utilizing dioxygen to degrade MTBE through a reductive activation process. The process occurs under reducing conditions. Therefore, it is possible to engineer a system where gasoline oxygenates can be oxidized through the reductive activation of dioxygen while chlorinated solvents can be reduced by taking advantage of reducing conditions. In other words, bifunctional aluminum has dual functionality of simultaneously decomposing oxidatively and reductively degradable contaminants. The ability to treat mixed contamination and the simple preparation procedures of bifunctional aluminum make it a promising remedial material for remediation of water contaminated with a wide array of contaminants. Moreover, the heterogeneous reaction system may be beneficial to *in situ* groundwater remediation; for example, a permeable reactive barrier composed of bifunctional aluminum could be implemented.

Acknowledgments

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