

Novel Bifunctional Aluminum for Oxidation of MTBE and TAME

Hsing-Lung Lien, A.M.ASCE,¹ and Weixian Zhang, M.ASCE²

Abstract: The transformation of methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME) using bifunctional aluminum in the presence of dioxygen (O₂) has been examined. Bifunctional aluminum, prepared by sulfating zero-valent aluminum with sulfuric acid, is an innovative extension of zero-valent metal technology. It has a dual functionality of simultaneously decomposing both reductively and oxidatively degradable contaminants. Bifunctional aluminum is capable of utilizing dioxygen through a reductive activation process to degrade oxygenates at ambient temperature and pressure where oxygenates are stable. The reductive activation of dioxygen is a new concept for oxygenate treatments for which most of oxidative technologies require strong oxidants. Results indicate that aluminum serves as a reductant to create favorable reducing conditions while sulfur-containing species, generated by the sulfation of aluminum at the metal surface, are considered to act as active sites. MTBE and TAME underwent similar parallel reaction pathways where the oxidation occurred on both sides of ether linkage. The oxidation of MTBE produced primarily *tert*-butyl alcohol, *tert*-butyl formate, methyl acetate, and acetone while *tert*-amyl alcohol, *tert*-amyl formate, methyl acetate, methyl ethyl ketone, and acetone accounted for 71.7% of the TAME lost. A postulated mechanism rationalizing the oxidation of oxygenates by bifunctional aluminum is proposed.

CE Database keywords: Aluminum; Organic chemicals; Oxidation; Water treatment; Oxygen.

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Introduction

Oxygenates such as methyl *tert*-butyl ether (MTBE) have been used as gasoline additives to reduce the level of carbon monoxide and volatile organic compounds from the emissions of motor vehicles since 1979. Rapid increase in MTBE use in the United States 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 (Johnson et al. 2000). However, due to leaking underground storage tanks and pipelines, the contamination of groundwater with oxygenates has become a growing concern. Studies conducted by the United States Geological Survey have shown that MTBE has quickly emerged as the second most frequently detected contaminant (after chloroform) in groundwater in the United States (Squillace et al. 1996). Groundwater contaminated with MTBE threatens public health because MTBE has tentatively been classified as a possible human carcinogen (Squillace

et al. 1997). The city of Santa Monica, utilizing groundwater as drinking water sources in California, has shut down a number of its drinking water wells since 1996 due to the presence of increasing levels of MTBE according to the California Environmental Protection Agency (Cal-EPA 1998).

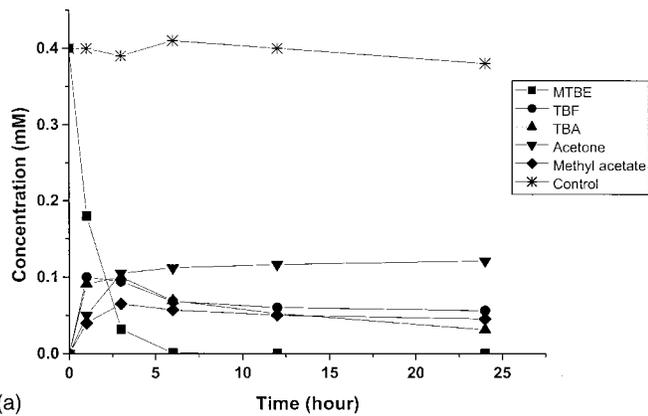
A number of technologies have been developed for the treatment of oxygenates. Conventional technologies such as granular activated carbon adsorption and air stripping have often been shown ineffective for MTBE removal (Speth and Miltner 1990; Squillace et al. 1997). On the other hand, advanced oxidation processes (AOPs) such as Fenton's reaction, ultraviolet (UV)/hydrogen peroxide, and ozone/hydrogen peroxide degraded MTBE effectively (vel Leitner et al. 1994; Chen et al. 1995; Liang et al. 1999; Stefan et al. 2000; Mitani et al. 2002). In general, AOPs involving the formation of highly reactive radical species (mainly hydroxyl radicals) require strong oxidants such as hydrogen peroxide and ozone as precursors and/or energy input (e.g., UV light).

Dioxygen (O₂) has been known as a very weak oxidant. Studies have shown that the direct oxidation of oxygenates such as *tert*-amyl methyl ether (TAME) by dioxygen occurs only at high temperature (Kadi and Baronnet 1995). In fact, even in the presence of strong oxidants such as ozone, the rate of the direct oxidation of MTBE is still very slow (Liang et al. 1999). However, a new possibility of using dioxygen for the oxidation through a reductive activation of dioxygen has been developed. The reductive activation of dioxygen involves the formation of reactive reduced oxygen species. The process has been found in enzyme systems such as mono-oxygenases (Sheldon 1994), bioinorganic systems (Akita and Moro-oka 1998), and O₂/H₂ fuel cells (Otsuka et al. 1990). Although the mechanisms for the dioxygen activation are complicated, this process can generally be expressed as Eq. (1) where [O] represents the reactive reduced oxygen species (Akita and Moro-oka 1998).

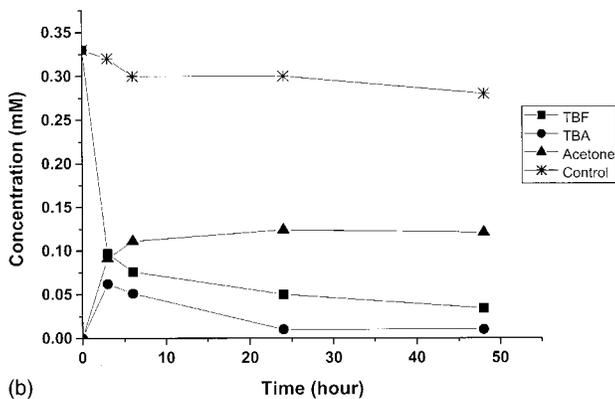
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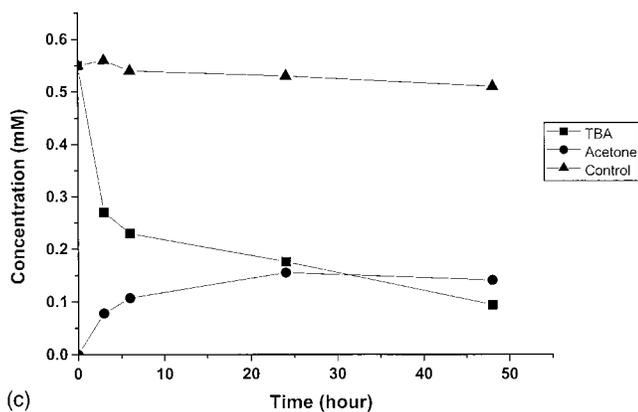
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(a)



(b)



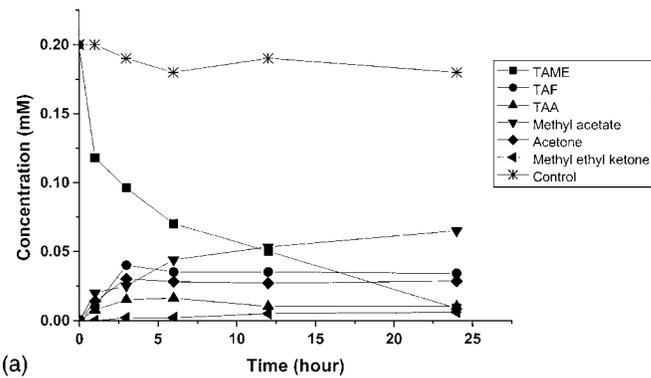
(c)

Fig. 1. Transformation of: (a) methyl *tert*-butyl ether, (b) *tert*-butyl formate, and (c) *tert*-butyl alcohol by bifunctional aluminum in presence of dioxygen

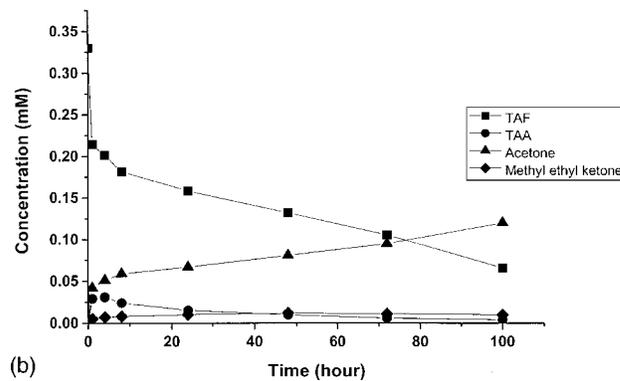
spectral patterns with those in the National Testing and Information Service Spectral Library. Standard chemicals were further used to verify the GC retention time and mass spectra. The detection limit of MTBE was determined to be less than 50 $\mu\text{g/L}$. Redox potential (Eh) and pH were measured with an Orion pH/mv meter equipped with a combination redox electrode and a combination pH electrode, respectively. The Eh readings were reported relative to the standard hydrogen electrode.

Results

The transformation of MTBE and TAME by bifunctional aluminum in the presence of dioxygen was conducted to investigate the



(a)

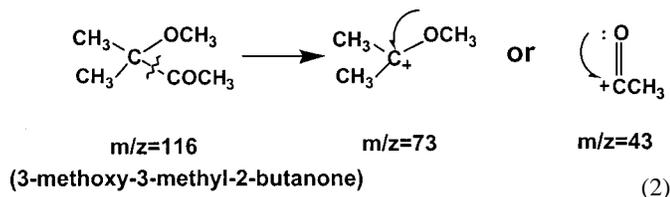


(b)

Fig. 2. Transformation of: (a) *tert*-amyl methyl ether and (b) *tert*-amyl formate by bifunctional aluminum in presence of dioxygen

effectiveness of bifunctional aluminum and to identify the intermediates. MTBE was rapidly degraded by bifunctional aluminum to TBF, TBA, methyl acetate, and acetone [Fig. 1(a)]. The mass balance of the MTBE oxidation at the end of the experiments was about 62%. The yields of TBF, TBA, methyl acetate, and acetone were about 13, 8.5, 11, and 29.2%, respectively. Isobutene, detected in minor amounts ($<1\%$), was positively identified by GC/MS. The Eh decreased from an initial value of +506 mv to -124 mv within 6 h. The measurement of Eh indicated that the batch system was operated under reducing conditions. The results for the transformation of TBF and TBA are shown in Figs. 1(b and c), respectively. Both showed slower degradation rates. The transformation of TBF produced TBA and acetone while the transformation of TBA produced only acetone. No methyl acetate was found in the transformation of either TBF or TBA.

Fig. 2(a) shows the time course of the product formation when reacting TAME with bifunctional aluminum. Intermediates, accounting for 71.7% of the TAME lost, included TAF, TAA, methyl acetate, acetone, and methyl ethyl ketone. Methyl propionate, β -isoamylene, and γ -isoamylene were detected in small amounts ($<1\%$). 3-Methoxy-3-methyl-2-butanone ($<1\%$) was tentatively identified in the TAME oxidation. The m/z values of this tentatively identified compound are 15 (44%), 29 (25%), 43 (100%), 57 (5%), and 73 (70%) where m/z 43 is the base peak. This compound has been identified in Schubert's study where only the base peak (m/z 43) was determined (Schubert 1991). Studies have also shown that the α -cleavage of 3-methoxy-3-methyl-2-butanone with respect to both functional groups resulting in charge retention by either fragment yields two oxonium ions (Butler 1964)



Although m/z 73 was determined as the base peak in the Butler's study, the difference of spectrum between Butler's study and this was within 30% acceptable error range (Raese et al. 1995).

The results for the transformation of TAF are illustrated in Fig. 2(b). The degradation intermediates included TAA, acetone, and methyl ethyl ketone. Acetone, accounting for approximately 38% of the TAF disappearance, was the major byproduct. A small amount of methyl ethyl ketone (3%) was also observed in the system and persisted to the end of the experiment. Notice that methyl acetate, methyl propionate, and 3-methoxy-3-methyl-2-butanone, which appeared in the transformation of TAME, were not detected in the transformation of TAF.

The transformation of MTBE and TAME to esters and ketones that indicates oxygenates undergo an oxidative degradation in reactions with bifunctional aluminum in the presence of dioxygen. Therefore, it is important to determine the role of dioxygen. Effects of dioxygen on the MTBE degradation by bifunctional aluminum are shown in Fig. 3. Dioxygen-free experiments were prepared by purging glass bottles with nitrogen gas (99.9%) for 45 min while dioxygen-rich experiments were carried out in batch bottles purged with pure oxygen gas (99.9%) for 1 min. The degradation of MTBE occurred only in the presence of both bifunctional aluminum and dioxygen. In the absence of bifunctional aluminum, the direct oxidation of MTBE by dioxygen did not proceed. In the absence of dioxygen, about 40% of initial MTBE was removed in the presence of bifunctional aluminum. This should be attributed to the sorption of MTBE onto the metal surface rather than the degradation because no intermediates such as TBF and TBA were found. The dioxygen dependence on the MTBE oxidation indicates dioxygen serves as a primary oxidant.

The capability of utilizing dioxygen by bifunctional aluminum for the oxidation of oxygenates at ambient temperature and pressure suggests a catalytic characteristic of bifunctional aluminum. Bifunctional aluminum with the sulfation treatment may create the active sites at the surface. The sulfation is a key step for the

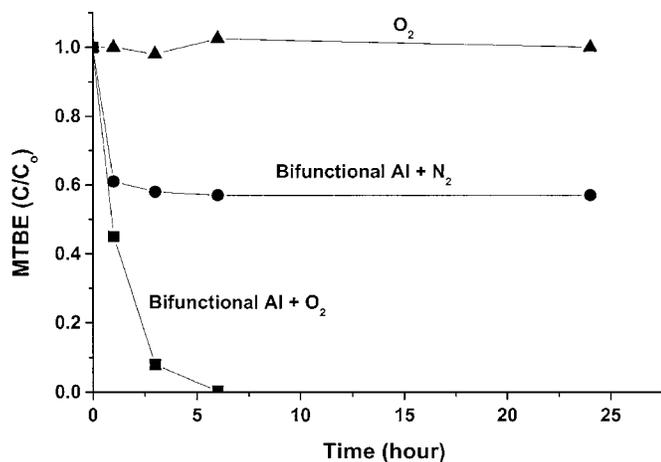


Fig. 3. Dioxygen dependence on methyl *tert*-butyl ether oxidation by bifunctional aluminum

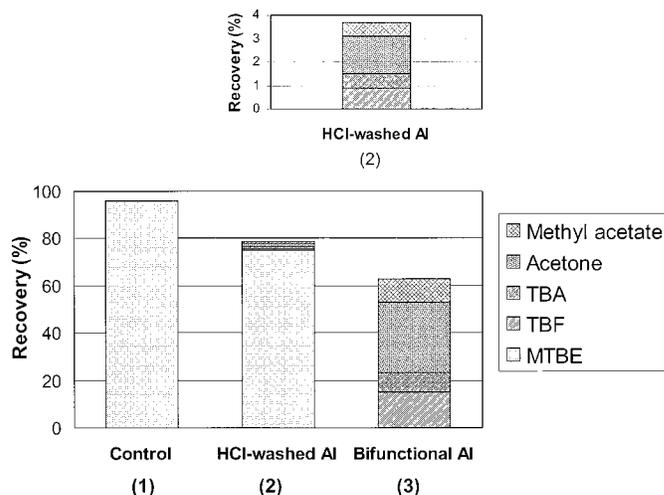


Fig. 4. Effect of sulfation on the promotion of aluminum for methyl *tert*-butyl ether oxidation. Recovery of methyl *tert*-butyl ether and its intermediates from methyl *tert*-butyl ether reacting with: (1) dioxygen alone, (2) HCl-washed aluminum with dioxygen, and (3) bifunctional aluminum with dioxygen. Inset shows minor products produced from reaction system (2).

synthesis of the so-called superacids such as sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) (Misono and Okuhara 1993). The superacid, exhibiting an acid strength greater than that of 100% H_2SO_4 , has widely been used as catalysts in many organic synthesis processes such as isomerization and alkylation. The catalytic capability of superacids has been attributed to the formation of catalytic sulfate species at the surface by the sulfation (Misono and Okuhara 1993; Song and Sayari 1996). In the case of bifunctional aluminum, the sulfation of aluminum resulting in the formation of the sulfur-containing species at the aluminum surface was found (Lien and Wilkin 2002).

To determine the importance of the sulfation, parallel experiments were conducted to compare the effectiveness of bifunctional aluminum and aluminum treated by HCl without sulfation (HCl-washed aluminum) in reactions with MTBE in the presence of dioxygen. As shown in Fig. 4, complete degradation of MTBE was found in the presence of bifunctional aluminum and only reaction intermediates (e.g., TBA, TBF) were observed in the system. However, approximately 75% of the initial MTBE remained in the batch system where only little oxidation of MTBE occurred by using HCl-washed aluminum. This indicates that the sulfation is an essential step to promote aluminum for utilizing dioxygen as the oxidant. Therefore, it is reasonable to believe that the surface sulfur-containing species generated by the aluminum sulfation could serve as active sites. It should be pointed out that a small amount of intermediates produced from MTBE reacting with HCl-washed aluminum was only found at the first sampling interval (1 h) (Fig. 4, inset). No further degradation of MTBE was observed after that. This provides an important insight into the role of aluminum that it serves as a reductant to create favorable reducing conditions. Under such conditions, the reduced oxygen species could be generated through the reductive oxidation of dioxygen. However, due to the lack of a sulfur-containing species, HCl-washed aluminum was unable to effectively utilize the reduced oxygen species for the MTBE oxidation because most of them would be consumed rapidly.

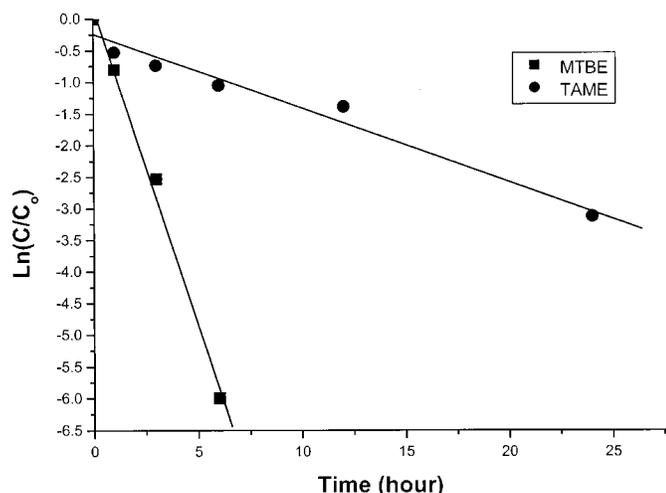


Fig. 5. Best fits of observed rate constants of methyl *tert*-butyl ether and *tert*-amyl methyl ether reacting with bifunctional aluminum

Discussion

Reaction Rates

The reaction kinetics of the transformation of MTBE, TAME, and their intermediates was modeled with a pseudo first-order rate equation

$$\frac{dC}{dt} = -k_{\text{obs}}C \quad (3)$$

where C = concentration of organic compounds in the aqueous phase (mg/L); k_{obs} = observed first-order rate constant (h^{-1}); and t = time (h). Batch experimental results in Figs. 1 and 2 were used to estimate the values of observed rate constants. For example, best fits of the experimental data to Eq. (3) were given in Fig. 5 for the reactions between bifunctional aluminum with MTBE and TAME. In Fig. 5, logarithmic values of the MTBE and TAME concentrations were plotted against time. Values of observed rate constants for other reactions are given in Table 1.

The disappearance of MTBE and TAME exhibited pseudo first-order behavior as shown in Fig. 5 ($R^2 > 0.96$), whereas poor correlation coefficients (R^2 between 0.64 and 0.90) indicated that the overall reaction of TBF, TBA, and TAF was not pseudo first-order (Table 1). In the cases of TBF, TBA, and TAF, similar trends were found: a fast initial disappearance of reactants followed by a slow subsequent degradation. This suggested that they underwent complex processes where sorption and reaction were involved together. Rates of sorption are a function of reactant concentration gradient. Fig. 3 shows a good example of the MTBE sorption behavior in the dioxygen-free batch system where the reaction of MTBE with bifunctional aluminum is negligible. The sorption occurred immediately when the batch system

Table 1. Values of Observed Rate Constants

Compound	k_{obs} (h^{-1})	R^2
MTBE	10.02×10^{-1}	0.9932
TAME	1.17×10^{-1}	0.9673
TBF	0.35×10^{-1}	0.6469
TBA	0.29×10^{-1}	0.8201
TAF	0.12×10^{-1}	0.8941

contained the highest initial concentration of MTBE in aqueous phase while quickly reaching steady state. Since the degradation state of TBA, TBF, and TAF was a slow process compared to that of MTBE and TAME, the quick decrease of initial concentrations caused by the sorption became a significant factor influencing the data linearization in accordance with pseudo first-order kinetics. As a result, the linearization of the measured data reflecting the mixed effects of sorption and reaction did not exhibit pseudo first-order behavior. Similar results have also been found in other slow reactions occurring in heterogeneous systems where sorption of organics was involved. For example, it has been reported that the transformation of tetrachloroethylene and trichloroethylene in a batch metallic iron–water system is not a simple pseudo first-order reaction but is a complex reaction involving a sorption and reductive degradation (Burris et al. 1995).

Reaction Pathways

The transformation of MTBE and TAME by bifunctional aluminum exhibited similar product patterns. For example, TAA, TAF, and isoamylenes from the TAME oxidation are analogous to TBA, TBF, and isobutene produced from the MTBE oxidation, respectively. This suggests that both undergo the same types of reaction pathways. Proposed degradation pathways of MTBE and TAME based on the detailed product studies are shown in Fig. 6. The MTBE oxidation proceeds via two parallel reaction pathways because methyl acetate was detected in the transformation of MTBE but was not found during the transformation of either TBF or TBA [Fig. 6(a)]. The major route of the MTBE transformation is via the oxidation of MTBE initiated at the methoxy group. This pathway leads to the conversion of MTBE to TBF, subsequently to TBA, and finally to acetone. The oxidation of MTBE initiated at the *tert*-butyl group is a minor pathway leading to the formation of methyl acetate.

The oxidation of MTBE to TBF by bifunctional aluminum is in good agreement with the documented oxidation pathways of ether to ester (Morrison and Boyd 1987; Barreto et al. 1995; Kang and Hoffmann 1998; Stefan et al. 2000; and Mitani et al. 2002). Esters such as TBF are subject to both acid and base catalyzed hydrolysis to yield carboxylic acids and alcohols (Morrison and Boyd 1987). At low pH, a rapid hydrolysis of TBF to TBA has been found (Church et al. 1999). In this study, we observed the hydrolysis of TBF to TBA, which is consistent with other studies on MTBE removal using advanced oxidation processes (Barreto et al. 1995; Mitani et al. 2002). In addition, TBF may undergo other reaction pathways. For example, Stefan et al. (2000) suggested a pathway (in radical reactions) to account for the formation of TBA from TBF degradation in the UV/H₂O₂ process.

tert-Butyl alcohol, a tertiary alcohol, contains no α -hydrogens and is less susceptible to the direct oxidation. However, under acidic conditions, the reversible dehydration of alcohol is a favorable reaction for tertiary alcohol (Morrison and Boyd 1987). The dehydration of TBA to isobutene in the presence of acidic catalysts such as Amberlyst 15 has been reported (Matouq and Goto 1993). The formation of isobutene has also been found in the photodegradation of MTBE with fly ash (Idriss and Seebauer 1996). A minor amount of dehydration products of tertiary alcohol was detected in the transformation of both MTBE and TAME with bifunctional aluminum. The observation of isobutene in this study suggests that a strong hydrogen donor group at the metal surface converts a poor leaving group ($-\text{OH}$) into a good leaving

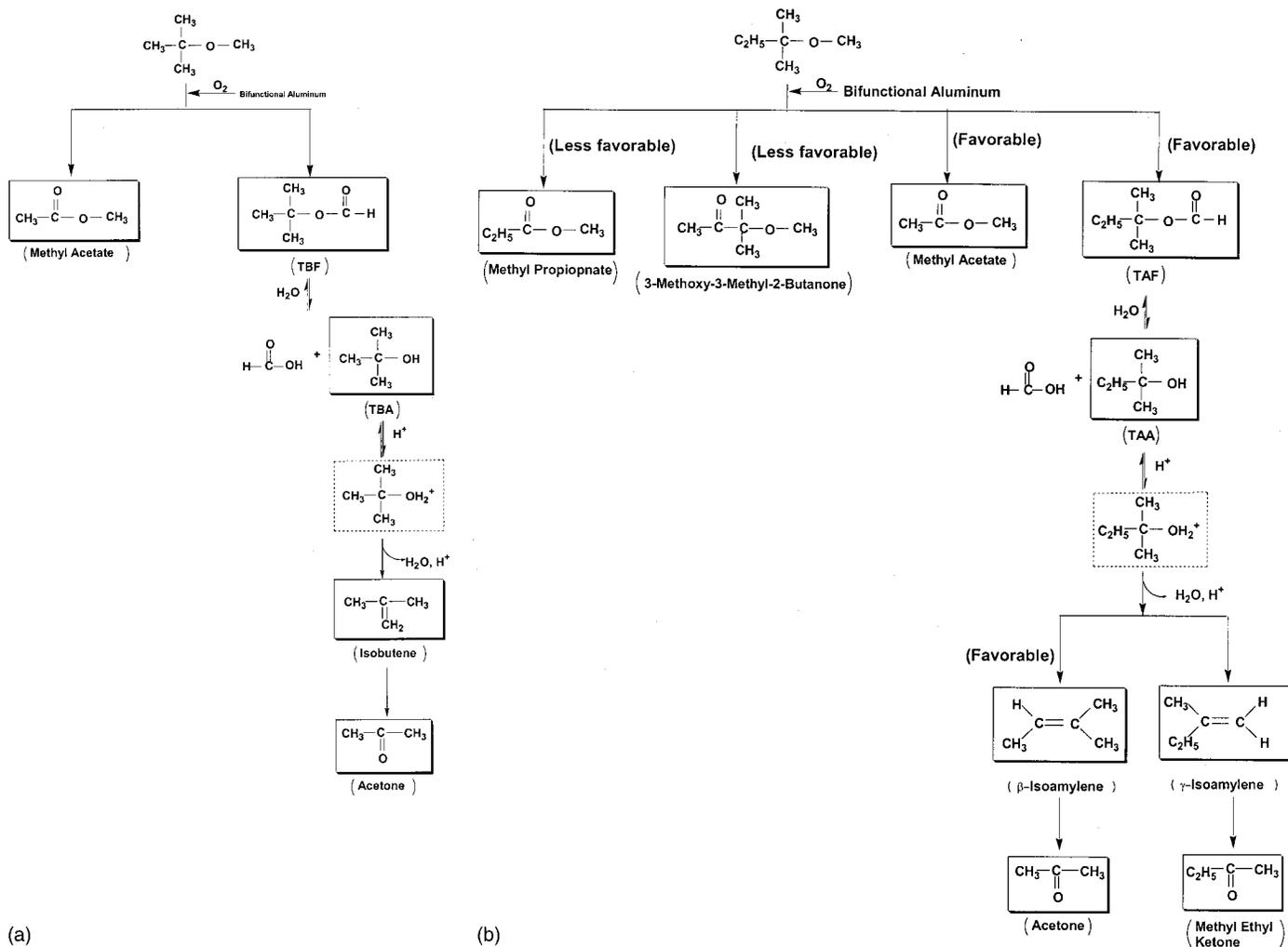


Fig. 6. Proposed reaction pathways for the (a) methyl *tert*-butyl ether and (b) *tert*-amyl methyl ether transformation by bifunctional aluminum in presence of dioxygen. Identified compounds are indicated with shaded boxes while suspected intermediates are shown with dotted boxes.

group ($-\text{OH}_2^+$) resulting in the TBA dehydration to isobutene. Isobutene was then oxidized to acetone. The addition of dioxygen to the double bond of alkenes leading to the formation of respective saturated ketones is one of the mildest electrophilic oxidations (Bielaski and Haber 1991).

Formation of methyl acetate could be attributed to the oxidation of MTBE initiated at the *tert*-butyl group. Photo-oxidation of MTBE to methyl acetate has been found in the gas phase studies where the formation of methyl acetate was attributed to hydroxyl radicals attacking at the *tert*-butyl group of MTBE (Japar et al. 1990; Smith et al. 1991). The attack on the *tert*-butyl side of ether was also demonstrated by the oxidation of di-*tert*-butyl ether, a symmetric ether with *tert*-butyl groups on both sides of the ether linkage (Langer et al. 1996). This study indicated that the *tert*-butyl group can be oxidized to acyl group in ethers. Analogously, methyl acetate containing an acyl group suggests that the oxidation of MTBE by bifunctional aluminum can proceed at the *tert*-butyl group.

Similar to the MTBE oxidation, the oxidation of TAME also proceeds via parallel reaction pathways [Fig. 6(b)]. The formation of TAF indicates that the oxidation of TAME initiated at the methoxy group is still a favorable route in the transformation of TAME. On the other hand, the formation of methyl acetate, 3-methoxy-3-methyl-2-butanone, and methyl propionate suggests

that the oxidation of oxygenates can occur at the functional groups on both sides of the ether linkage. This is consistent with the MTBE study. Based on the molecular structure of TAME, the ethyl group on the *tert*-amyl side provides more reactive sites to attack for the TAME oxidation. Cleavage of the ethyl and methyl group leads to the formation of methyl acetate, while the scission of two methyl groups leads to the formation of methyl propionate. The oxidation of C-H bonds at the ethyl group of the *tert*-amyl side provides a reaction pathway to 3-methoxy-3-methyl-2-butanone.

Analogous to TBF, TAF produced via the oxidation of TAME at the methoxy group can also undergo the hydrolysis to TAA. The dehydration of TAA led to the formation of isoamylenes including β -isoamylene and γ -isoamylene. The formation of isoamylene isomers exhibited Saytzeff orientation that a multi-substituted alkene product is preferred over a monosubstituted one from the dehydration reaction (Morrison and Boyd 1987). β -Isoamylene with three alkyl groups attached to the doubly bonded carbon atoms is more stable than γ -isoamylene, which has only two alkyl groups attached to the carbon atoms. Although both isomers were detected in trace amounts, the further oxidation of β -isoamylene and γ -isoamylene to acetone (14.2%) and methyl ethyl ketone (3%), respectively, indicates that β -isoamylene is the preferred product.

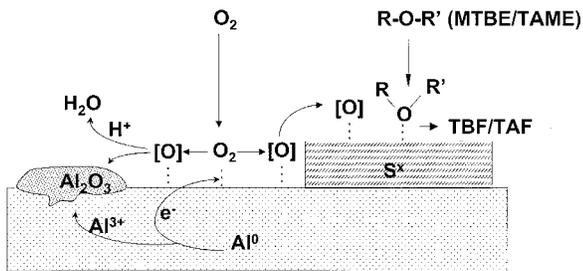


Fig. 7. Conceptual model accounting for roles of aluminum, surface sulfur-containing species (S^x), dioxygen, and reduced oxygen species ($[O]$) in oxidation of oxygenates

Postulated Mechanism

Because MTBE and TAME are stable at ambient temperature and pressure, the capability of activating dioxygen by bifunctional aluminum for the oxidation of oxygenates under reducing conditions suggests that the reaction involves the reductive activation of dioxygen. Recently, we have reported that the simultaneous oxidation of MTBE and reduction of carbon tetrachloride can occur by using bifunctional aluminum in the presence of dioxygen (Lien and Zhang 2000). At first sight, the oxidation of MTBE requiring an electron acceptor sounds incompatible with the reduction of carbon tetrachloride requiring an electron donor in the same system. However, the reductive activation of dioxygen by bifunctional aluminum under reducing conditions, where the reductive degradation is also a favorable process, rationalized this result. A postulated mechanism for the oxidation of oxygenates by bifunctional aluminum is illustrated in Fig. 7.

Aluminum metal with a strong reduction potential (-1.667 V) converts dioxygen into the reactive reduced oxygen species at the surface through an electron transfer. The reduced oxygen species are nonselective strong oxidants. In general, they would be rapidly consumed by aluminum or further reduce to water before oxidizing oxygenates. Nevertheless, the sulfur-containing species at the aluminum surface act as the active sites that stabilize the reduced oxygen species. The oxidation of oxygenates by the reduced oxygen species can therefore occur when oxygenate molecules adsorb onto the surface of bifunctional aluminum.

Conclusions

A novel bifunctional aluminum that was prepared by sulfating aluminum metal with sulfuric acid effectively degraded gasoline oxygenates using dioxygen as the oxidant. Gasoline oxygenates were oxidized through the reductive activation of the dioxygen process. The process occurred in the bifunctional aluminum system where aluminum serves as the strong reductant to create favorable reducing conditions. The sulfation, leading to the formation of sulfur-containing species at the metal surface, is a key step in the preparation of bifunctional aluminum. The sulfur-containing species are considered to act as active sites for the stabilization of the reduced oxygen species. Bifunctional aluminum is an innovative extension of zero-valent metal technology that has widely been used for groundwater remediation in association with permeable reactive barriers. This work demonstrates that bifunctional aluminum is a reactive remedial reagent for the treatment of gasoline oxygenates in heterogeneous systems. Because of the potential for serving as a reactive media in permeable

reactive barriers, bifunctional aluminum could be developed as a promising strategy for remediation of groundwater contaminated with gasoline oxygenates. Crucial application considerations still remain, however, such as effects of environmental factors on long-term performance of bifunctional aluminum, optimization of the synthetic process, and optimum dosing of dioxygen requirements. Current research efforts are focused on these issues.

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