Gas-phase photocatalytic oxidation of motor fuel oxygenated additives

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Abstract Methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) were oxidized in the gas phase by photocatalytic oxidation (PCO). Transient PCO was carried out at room temperature on TiO2 (Degussa P25), 0.2% Pt-TiO2, and 2% Pt-TiO2 catalysts. Surface-adsorbed reaction by-products were characterized by temperature-programmed desorption (TPD) and oxidation (TPO). Continuous flow PCO was also carried out at 373 K on TiO2. Acetone, H2O, and CO2 were the gas-phase products for PCO of TBA and MTBE, and formic acid was adsorbed on the TiO2 surface. Temperature-programmed desorption of TBA and MTBE formed 2-methyl-1-propene, water (TBA), and methanol (MTBE). During continuous-flow PCO, acetone desorbed in molar amounts equal to the amount of decomposed TBA and MTBE. The Pt/TiO2 catalysts had higher rates of complete oxidation during PCO and TPO. Injection of water during transient PCO increased the rates of oxidation of adsorbed TBA, formic acid, and acetone. Photocatalytic oxidation of TBA proceeded faster in humid air than dry air, but MTBE oxidation was less sensitive to humidity. The TiO2 catalyst was stable for MTBE, TBA, and acetone PCO at 373 K. The PCO at low conversions followed the Langmuir–Hinshelwood model.

Keywords Gas-phase photocatalytic oxidation; methyl tert-butyl ether; tert-butyl alcohol

Introduction

Due to massive production of methyl tert-butyl ether (MTBE) in the 1990s, significant amounts of MTBE are in subsurface water as a result of storage tank and pipeline leaks and gasoline spills (Johnson et al., 2000). In the current study, the mechanism and kinetics of PCO of MTBE over TiO2 were studied in the gas phase by both transient and continuous flow methods. Tert-butyl alcohol (TBA), acetone, and formic acid were also studied: TBA forms by hydrolysis of MTBE, and the others are by-products of PCO of both MTBE and TBA.

Photocatalytic oxidation (PCO) in the aqueous phase is possible (Barreto et al., 1995), but the high volatility of MTBE and the slow rate of PCO in the liquid phase make gas-phase PCO studies more promising. Air stripping is a reliable technology to remove VOCs from groundwater, but needs additional pervaporation equipment for MTBE (Keller and Bierwagen, 2001). The MTBE-laden air has to be treated before release to the atmosphere. A few studies have reported PCO of vapor-phase MTBE (Raupp and Junio, 1993; Idriss et al., 1997; Alberici and Jardim, 1997), although little information is available on the kinetics and the composition of PCO products.

Experimental methods

A thin-film annular reactor was used for the transient PCO. Catalyst was coated onto the Pyrex glass using a procedure described previously (Larson et al., 1995). The reactor was surrounded by a transparent furnace and twelve 8-W black light bulbs surrounded the furnace. The three reactors used were coated with TiO2 (Degussa P25, 45 mg), 0.2% Pt-TiO2.
(30 mg), and 2% Pt-TiO₂ (30 mg). The VOC was adsorbed onto the catalyst to saturation at room temperature by injecting the liquid upstream and allowing it to evaporate into a 20% O₂/He stream (100 cm³/min). Reaction was carried out at room temperature by turning the UV lights on. The gas-phase species were analyzed by a Balzers QMA 125 quadrupole mass spectrometer. In order to detect reaction products that remained adsorbed on the surface, temperature-programmed desorption (TPD) in a He stream and temperature-programmed oxidation (TPO) in a 20% O₂/He was carried out after PCO was stopped by turning off the lights. The heating rate was 1 K/s to 723 K.

A simple annular reactor was used for continuous flow PCO. To build the reactor, a 15-W low-pressure mercury tube (maximum radiation intensity at 365 nm) was coaxially inserted into a glass tube. The ends were sealed around the lamp, allowing gas flow through the annular space. The reactor walls were coated with a TiO₂ (Degussa P25) layer from aqueous slurry. The reactor was 36 cm long, the annular gap was 3.3 mm, and the outer diameter of the lamp was 25 mm. Approximately, 0.89 g of TiO₂ coated about 640 cm² of the reactor. An evacuated gas cylinder was filled with the desired amount of VOC through an injection port, and it was then filled with synthetic air (20% O₂, 80% N₂). The VOC-containing stream was blended with a diluent gas stream to deliver the desired VOC concentration to the reactor. The reactor was held at 373 K, which is the temperature normally achieved from the heat of the lamp for an airflow rate up to 3 L/min. The products were analyzed by a Perkin Elmer 2000 FT-IR spectrometer with Sirocco 10.6-m gas cell.

Results and discussion

Transient PCO of TBA. TBA readily oxidized on the UV-irradiated TiO₂ catalyst surface. Acetone, water and CO₂ were the main gas phase products during transient PCO of TBA (Figure 1). Traces of formic acid were also detected. More TBA adsorbed on Pt/TiO₂ than on TiO₂. The Pt/TiO₂ catalysts also oxidized TBA more completely; only half as much acetone formed on the Pt/TiO₂ catalysts even though they adsorbed more TBA, and much more CO₂ formed. The composition of PCO products that remained adsorbed on the Pt/TiO₂ catalysts was also quantitatively different, as determined by TPD after PCO.

Formic acid was observed during PCO on TiO₂ and during the subsequent TPD as it decomposed to form CO at 610 K (Muggli et al., 1998). Acetone and 2-methyl-1-propene were also seen during TPD after PCO. 2-Methyl-1-propene was also seen during TPD of a saturated layer of TBA, although acetone was not. Thus, 2-methyl-1-propene is probably a decomposition product of TBA that did not react during PCO, and acetone is a product that remained adsorbed when TBA was oxidized photocatalytically. The CO₂ that desorbed at 723 K is characteristic of adsorbed acetone (Larson et al., 1995).

![Figure 1](https://iwaponline.com/wst/article-pdf/49/4/141/420752/141.pdf)  
**Figure 1** PCO products of TBA on TiO₂  

![Figure 2](https://iwaponline.com/wst/article-pdf/49/4/141/420752/141.pdf)  
**Figure 2** PCO products of MTBE on TiO₂
Transient PCO of MTBE. The MTBE coverages were 60–70% of the TBA coverages and were the same on the three catalysts. Carbon dioxide and water were the main PCO products on TiO₂, and in contrast to PCO of TBA, only a small amount of acetone was seen (Figure 2). The rates and amounts of CO₂ formed during PCO were higher on the Pt/TiO₂ catalysts, and thus the amount of products that formed during the subsequent TPD/TPO was smaller. Formic acid was on the TiO₂ surface after PCO since CO from formic acid decomposition was observed during TPD following PCO of MTBE.

The same volatile products were observed for PCO of MTBE on Pt/TiO₂ as seen on TiO₂. During TPD following PCO, however, CO₂ was the main product on Pt/TiO₂ and the CO did not correspond to formic acid decomposition: formic acid decomposes on Pt/TiO₂, with a maximum desorption temperature around 525 K, to form CO₂, CO, and H₂ in almost equal amounts (Blount et al., 2001). No hydrogen was detected and no CO₂ and CO peaks formed at 525 K. The amount of products adsorbed on Pt/TiO₂ after PCO was small, indicating more complete oxidation.

Transient PCO of acetone. Transient PCO of acetone on TiO₂ was studied in detail by Larson et al. (1995), and similar results were obtained in the current study. Carbon dioxide and CO were the main products, and trace amounts of formic acid also formed. A subsequent TPD showed that formic acid remained on the surface and decomposed to CO and small amounts of CO₂ around 573 K.

Continuous-flow PCO. During continuous-flow PCO at 373 K of TBA and MTBE, CO₂ and acetone products were observed, and conversions were less than 100%. Trace amounts of CO were detected. Carbon monoxide was also detected during acetone PCO. When the reactor was exposed to the VOCs at 373 K in the absence of UV light, no decomposition was observed. That is, all the reaction in the presence of UV light was due to PCO and no thermal catalytic reaction took place at 373 K. For an MTBE concentration of 400 ppmv, the rate of PCO did not change during more than 100 h on stream. Photocatalytic oxidation of MTBE, TBA, and acetone in the absence of water for about 8 months for a few hours daily showed no decrease in the photocatalyst activity. The conversion during PCO depended on the contact time and feed concentrations.

The carbon mass balance for PCO was within ±7% for TBA and ±2–3% for MTBE and acetone. At the short contact times, all the reacted MTBE and TBA was stoichiometrically converted to acetone; the additional carbon in MTBE and TBA was oxidized to CO₂. At longer contact times, acetone oxidized so that the one mole of acetone was not detected for every mole of MTBE or TBA reacted. Instead, CO₂ and CO formed.

The amount of acetone that formed during continuous flow PCO was equal to the amount of MTBE that decomposed, whereas acetone only formed in trace amount during transient PCO of MTBE. In contrast, a large amount of acetone formed during transient PCO of TBA. This may be explained by the difference in by-products formed during PCO of TBA and MTBE. Water presumably forms directly as a result of PCO of TBA, and this water displaces weakly adsorbed acetone. For PCO of MTBE, water forms after decomposition of formic acid, which is produced from methyl groups at longer times. Thus the adsorbed acetone has more time to react. During continuous flow PCO of MTBE, the continuous supply of MTBE could displace acetone from the surface. Indeed, when MTBE was pulsed over illuminated TiO₂ in air, acetone desorbed in a pronounced peak at the same time as MTBE was observed.

Decomposition rate. The percent conversion of MTBE, TBA, and acetone decreased as the VOC inlet concentration increased. This indicates that the reactions are neither first-order nor diffusion-controlled. The results were consistent with Langmuir–Hinshelwood (L–H) kinetics:
or

\[ \frac{1}{r_0} - \frac{1}{kK} \frac{1}{C_{in}} + \frac{1}{k} \]

where \( k \) is the L–H rate constant and \( K \) is the Langmuir adsorption coefficient.

Figure 3 shows the approximately linear dependence when plotted according to Eq. (2). The kinetic parameters \( k \) and \( K \) in Table 1 were obtained using linear least squares analysis. TBA was the most reactive of the three VOCs and it had the highest rate constant; acetone was the least reactive. MTBE has the highest Langmuir adsorption coefficient (Table 1), and thus it oxidized twice as fast as acetone even though their rate constants were similar. Initial PCO rates per gram of catalyst (\( \mu \text{mol g}^{-1} \text{ catalyst s}^{-1} \)) ranged from 0.03 to 0.08 for MTBE, 0.06 to 0.20 for TBA and 0.02 to 0.036 for acetone. Rates per unit area covered with \( \text{TiO}_2 \) were (\( \mu \text{mol m}^{-2} \text{s}^{-1} \)) 0.45 to 1.1, 0.80 to 2.80 and 0.17 to 0.50, respectively.

**Effect of humidity.** During a transient PCO, water injection increased the rate of TBA oxidation, although it also increased acetone desorption. Similarly, water injection increased the rate of acetone and formic acid PCO: the desorptions of adsorbed substances and CO\(_2\) were accelerated. This could be explained by accelerated oxidation of adsorbed VOC and oxidation of by-products. Water injection only slightly enhanced CO\(_2\) formation during MTBE transient PCO.

Photocatalytic oxidation of TBA under continuous flow proceeded faster in humid air than dry air at 373 K for TBA concentrations from 50 to 300 ppmv and RH values from 20 to 85% (25°C).

Measurements with FTIR of the MTBE concentrations in humid air were only accurate up to 20 % RH (25°C) due to the interference of water vapors. Continuous flow PCO of MTBE in humid air was, in contrast to TBA, practically independent of RH; the PCO rate slightly decreased.

The difference in the influence of humidity on PCO of TBA and MTBE may be

![Figure 3](https://iwaponline.com/wst/article-pdf/49/4/141/420752/141.pdf)

**Figure 3** Langmuir–Hinshelwood plots of the reciprocal of the initial PCO rate vs. the reciprocal of the VOCs’ inlet concentrations for TiO\(_2\) catalyst

**Table 1** Langmuir–Hinshelwood parameters for PCO of MTBE, TBA and acetone on TiO\(_2\) at 373K

<table>
<thead>
<tr>
<th>VOC</th>
<th>( k \times 10^3 ), ( \text{mol m}^{-2} \text{s}^{-1} )</th>
<th>( K, \text{m}^2 \text{mol}^{-1} )</th>
<th>( kK, \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE</td>
<td>0.8 ± 0.02</td>
<td>470 ± 10</td>
<td>0.4 ± 0.01</td>
</tr>
<tr>
<td>TBA</td>
<td>3.2 ± 0.2</td>
<td>200 ± 20</td>
<td>0.6 ± 0.05</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.5 ± 0.05</td>
<td>200 ± 20</td>
<td>0.1 ± 0.01</td>
</tr>
</tbody>
</table>
explained by different adsorption strengths of these two substances relative to water. MTBE is easily displaced by water, whereas TBA is not. Therefore, the increase in the reaction rate caused by the presence of humidity is compensated by partial desorption of MTBE so that the PCO rate did not change much with humidity. In contrast, PCO of TBA benefited from humidity because water increased the rate and it did not desorb TBA.

Conclusions
Gas-phase MTBE and TBA oxidize photocatalytically on TiO$_2$ and Pt/TiO$_2$ catalysts. Acetone, H$_2$O, and CO$_2$ were the main oxidation products. Formic acid was an intermediate that remained adsorbed on the surface of TiO$_2$. Continuous-flow PCO converted TBA and MTBE to acetone stoichiometrically at low conversions; acetone was displaced from TiO$_2$ by TBA and MTBE. Formic acid, an oxidation intermediate of TBA and MTBE, did not desorb and was converted to CO$_2$ and H$_2$O. TBA oxidized faster than MTBE and acetone.

Pt/TiO$_2$ catalysts had higher rates of PCO. A formic acid intermediate did not accumulate on Pt/TiO$_2$ and was oxidized to CO$_2$ and H$_2$O. Water increased the transient PCO rate of adsorbed TBA, acetone, and formic acid. Continuous-flow PCO of TBA was enhanced in presence of humidity, whereas MTBE was less sensitive to water vapor. The TiO$_2$ catalyst was stable during PCO of MTBE, TBA, and acetone at 373 K. At low conversions under the conditions used, PCO followed Langmuir–Hinshelwood kinetics.

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