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The dependence on temperature of gas-phase photocatalytic oxidation of methyl *tert*-butyl ether and *tert*-butyl alcohol

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Abstract

The influence of temperature on the mechanism and kinetics of gas-phase photocatalytic oxidation (PCO) and thermal oxidation (TO) of methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA) over TiO_2 was studied in a continuous flow annular reactor. The reaction products of PCO of both substances included acetone, water, carbon dioxide and carbon monoxide. Volatile TO products of MTBE included 2-methyl-1-propene (2-MP), carbon monoxide, carbon dioxide and water; TBA decomposed to 2-MP and water. Thermal oxidation of MTBE became noticeable at 388 K, TBA started to decompose thermally at 393 K. Both PCO and TO fit well to the Langmuir–Hinshelwood (L–H) model for monomolecular reactions. The dependence of the kinetic constants on temperature was established in the form of an Arrhenius equation. The TiO_2 catalyst showed no deactivation at temperatures above 373 K but gradually lost its activity below 373 K.

Keywords: Photocatalytic oxidation; Thermal oxidation; Methyl *tert*-butyl ether; *tert*-Butyl alcohol; Titanium dioxide

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1. Introduction

Methyl *tert*-butyl ether (MTBE) was the most widely used motor fuel additive in the USA until 1998 and is still the basic oxygenated additive used nowadays in the rest of the world. As a result of massive production of MTBE significant amounts are found in groundwater because of storage tank and pipeline leaks and fuel spills [1]. *tert*-Butyl alcohol (TBA) has been reported as a primary product of photocatalytic degradation and hydrolysis of MTBE in aqueous media [2,3]. Photocatalytic oxidation (PCO) in the aqueous phase is a viable process for elimination of MTBE [2,4], but the slow rate of PCO in the aqueous phase makes gas-phase PCO studies more promising. Air stripping is a reliable technology to remove volatile organic compounds (VOCs) from groundwater, but needs additional pervaporation equipment for MTBE [5]. The MTBE-laden air has to be treated before release to the atmosphere. A few studies have reported PCO of vapour-phase MTBE [6–8], although little information is available on the PCO kinetics and its dependence on temperature.

In the present research, MTBE and TBA oxidation on a TiO_2 surface was studied in its photocatalytic mode with UV-radiation, as was thermal decomposition in the dark within a temperature range of 333–453 K.

2. Experimental methods

The gas-phase PCO of MTBE and TBA over UV-illuminated TiO_2 was studied using an annular photocatalytic reactor in continuous gas-flow mode, having an inner diameter 32 mm, total volume 0.105 L, annular gap (between the lamp and inner wall of the reactor) 3.5 mm, outer diameter of the lamp 25 mm. A 365 nm 15 W low-pressure mercury luminescent UV-lamp was positioned coaxially in the reactor. The reactor assembled with the lamp was coated inside with TiO_2 (Degussa P25) by a 50-times rinse with a TiO_2 aqueous suspension, each rinse followed by drying. Approximately, 0.89 g of TiO_2 coated about 640 cm^2 of the reactor (1.4 mg cm^{-2}). The irradiance of the

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TiO_2-coated UV-lamp was measured with a UVX Radiometer at the surface next to the lamp and averaged about 0.6 mW cm^{-2} in a 365-nm range.

An evacuated gas cylinder was filled through an injection port with the desired amount of VOC, and then filled with synthetic air (20% O_2, 80% N_2). The VOC-containing stream was blended with a diluent gas to deliver the desired VOC concentration to the reactor. The temperature in the reactor was varied from 333 to 453 K at a gas flow rate 3.5 L min^{-1}, which made the contact time equal to 1.8 s. This detention time was sufficient to reliably register the difference between VOC concentrations in the inlet and outlet streams, keeping that difference within a few ppmv limits to avoid complications caused by intermediate by-products. The temperature was adjusted with heating tape wrapped around the reactor. The tape was controlled with a temperature regulator (Omega CN9000A with a K-type thermocouple). For an airflow rate up to 3.5 L min^{-1}, the lamp heated the insulated reactor to 373 K. Lower temperatures were obtained by removing insulation. The reaction products were analyzed by a Perkin Elmer 2000 FT-IR spectrometer with Sirocco 10.6 m gas cell. Since the volume of the cell was 3.6 L, the time of sampling was 10–15 min for proper averaging. Outlet stream samples were taken three to six times during the 150 min run. Thermal oxidation (TO) of MTBE and TBA was conducted in the same reactor, without UV-radiation, at temperatures from 373 to 453 K. Inlet concentrations of VOC pollutants varied from 20 to 300 ppmv (9×10^{-4} to 1.33×10^{-2} mol L^{-1}). No humidity was introduced to the air stream.

3. Results and discussion

3.1. PCO and TO products

All the reacted TBA and MTBE were stoichiometrically converted to acetone (Eqs. (1) and (2)) [9]; the additional carbon in TBA and MTBE molecules was oxidized to CO_2 (Eq. (3)) along the reactions:

$$\underset{\text{TBA}}{(CH_3)_3C{-}OH} \overset{h^+,O_2}{\Rightarrow} \underset{\text{Acetone}}{(CH_3)_2C{=}O} + H_2O + CH_3\cdot \quad (1)$$

$$\underset{\text{MTBE}}{(CH_3)_3C{-}O{-}CH_3} \overset{h^+,O_2}{\Rightarrow} \underset{\text{Acetone}}{(CH_3)_2C{=}O} + 2CH_3{}^{\bullet} \quad (2)$$

$$CH_3{}^{\bullet} \overset{h^+,O_2}{\Rightarrow} \underset{\text{Formic acid}}{HCOOH} \overset{h^+,O_2}{\Rightarrow} CO_2 + H_2O \quad (3)$$

Partial oxidation of acetone resulted in formation of CO [9].

The products of TO of MTBE included 2-methyl-1-propene (2-MP) in a stoichiometric one-to-one ratio with the decomposed MTBE (Eq. (4)). The metoxy-group in the MTBE molecule was thermally oxidised to carbon dioxide and monoxide through the stages of formation of methanol and subsequently formic acid, observed in transient studies elsewhere (Eq. (5)) [9]. TBA decomposed to 2-MP and water with no trace of any other carbonaceous products (Eq. (6)):

$$\underset{\text{MTBE}}{(CH_3)_3C{-}O{-}CH_3} \overset{\text{Heat}}{\Rightarrow} \underset{\text{2-MP}}{(CH_3)_2C{=}CH_2} + CH_3OH \quad (4)$$

$$CH_3OH \overset{\text{Heat},O_2}{\Rightarrow} \underset{\text{Formic acid}}{HCCOH} \overset{\text{Heat},O_2}{\Rightarrow} CO + CO_2 + H_2O \quad (5)$$

$$\underset{\text{TBA}}{(CH_3)_3C{-}OH} \overset{\text{Heat}}{\Rightarrow} \underset{\text{2-MP}}{(CH_3)_2C{=}CH_2} + H_2O \quad (6)$$

3.2. PCO and TO kinetics

Fig. 1 shows the conversions of MTBE and TBA as a result of PCO versus inlet reactant concentrations and temperatures. The conversion varies inversely with the inlet reactant concentration at all temperatures. This kinetic behaviour indicates that the surface reactions are unlikely to be elementary ones: a diffusion-controlled reaction or elementary first order reaction would exhibit constant conversions versus inlet concentration [10].

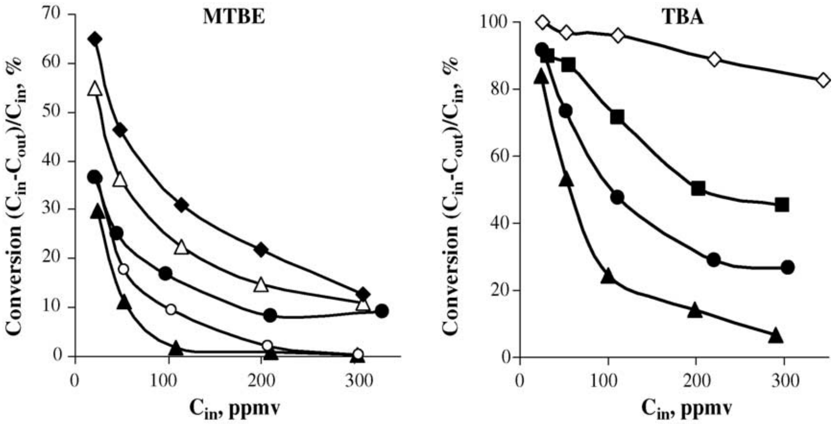

Fig. 1. PCO/TO conversions of MTBE and TBA vs. their inlet concentrations at different temperatures: (▲) 333 K, (○) 353 K, (●) 373 K, (△) 388 K, (◆) 403 K, (■) 413 K, (◇) 453 K.