

Mechanistic Study of CH₃OH + O₂ Photoredox Reaction in a FeAlPO₄ Sieve by Time-Resolved FT-IR Spectroscopy[†]

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The mechanism of the ligand-to-metal charge transfer (LMCT) induced reaction of methanol and O₂ at the gas–micropore interface of a FeAlPO₄-5 sieve has been studied by time-resolved FT-IR spectroscopy. Measurements using the rapid-scan method revealed that the final products, HCO₂⁻···Fe and H₂O, emerge with a rise time of 4 s (250 K) by decomposition of the two-electron-transfer intermediate, HO₂CH₂OH. Intermediacy of hydroxymethylhydroperoxide was established by direct detection by step-scan FT-IR spectroscopy on the 500 microsecond time scale and by monitoring of its photodissociation products HCO₂H + H₂O on the millisecond and second time scale. Formaldehyde was observed as minor two-electron oxidation product. The fast rise of the HO₂CH₂OH intermediate strongly suggests that it is formed by direct coupling of HOO and CH₂OH radicals. This constitutes the most conclusive evidence yet for the formation of a hydroperoxy radical and hydroxymethyl radical as the primary one-electron-transfer products of the reaction of CH₃OH and O₂ at LMCT-excited framework Fe centers.

I. Introduction

Substantial progress in the understanding of the multistep processes following interaction of donor and acceptor molecules with excited framework metals of molecular sieves is expected from in situ time-resolved monitoring of the chemistry. To obtain insight into the detailed mechanism of a prototypical redox reaction in a microporous material, we have employed rapid-scan and step-scan FT-IR spectroscopy to follow CH₃-OH oxidation and O₂ reduction in a ligand-to-metal charge transfer (LMCT) excited Fe aluminophosphate sieve. A recent study in our laboratory of the 355 nm induced reaction of CH₃-OH and O₂ gas adsorbed on FeAlPO₄-5 by static FT-IR spectroscopy gave formate (HCO₂⁻···Fe) and water as four-electron-transfer products.¹ Methyl formate emerged on a much longer time scale-upon condensation of HCO₂H with excess CH₃OH. Monitoring of the reaction on the millisecond and second time scale is expected to reveal the rise of these products and, possibly, the formation of two-electron-transfer intermediates such as formaldehyde and hydrogen peroxide proposed earlier.¹ No CH₂=O was observed by static FT-IR spectroscopy despite its intense infrared bands, even when conducting the photochemistry at -100 °C. Our study of the adducts of the aldehyde with various species present upon methanol + O₂ reaction (H₂O, H₂O₂, CH₃OH, and lattice OH groups), reported in the preceding paper,² indicates that only hydroxymethylhydroperoxide, the addition product of CH₂=O and H₂O₂, is sufficiently labile in the dark and under irradiation for playing a possible role as a two-electron-transfer intermediate. The molecule was found to dissociate in a FAPO-5 sieve in the dark or upon 355 nm excitation to HCO₂H (HCO₂⁻···Fe) and H₂O.²

In this paper, we report time-resolved FT-IR measurements on the microsecond to second time scale in order to elucidate the mechanism of the methanol + O₂ photoredox chemistry in the LMCT-excited FeAlPO₄-5 sieve.

II. Experimental Section

Self-supporting FeAlPO₄-5 wafers (AFI structure, abbreviated FAPO-5) were prepared and mounted in a miniature infrared vacuum cell as described in the preceding paper.² The infrared cell was mounted inside an Oxford model DN1714 cryostat. After dehydration at 473 K overnight under high vacuum, the temperature of the sieve was lowered for loading with 5 Torr of methanol and 700 Torr of O₂ (or N₂). Time-resolved photolysis experiments were conducted at 250 K unless noted otherwise.

Rapid scan FT-IR measurements^{3,4} were conducted with a Bruker model IFS88 spectrometer. A highly sensitive HgCdTe photon detector Kolmar model KMPV8-1-J2 with an 8 micron band gap was used ($D^* = 1 \times 10^{11}$ cm Hz^{1/2} W⁻¹). To maximize the sensitivity for spectroscopy in the fingerprint region, folding limits were chosen at 2106 and 1054 cm⁻¹ requiring an infrared filter for blocking off probe light outside this range (OCLI model W07100-11X). Reaction was initiated by 355 nm nanosecond pulses (third harmonic) of either a Nd:YAG laser Coherent model Infinity or Quanta Ray model DCR2A (with GCR-3 upgrade). A small quartz prism (1 cm edge-to-edge) was used to align the photolysis beam collinearly with the infrared probe beam. To prevent photolysis light entering the detector or interferometer compartment, the ports to these compartments were closed off by 2 in. germanium plates with dielectric coatings that maximized infrared transmission ($T = 95\%$, International Scientific).

Experiments were conducted on the millisecond and second time scale. One method for obtaining millisecond spectra

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