



Catalytic thiophene oxidation by groups 4 and 5 framework-substituted zeolites with hydrogen peroxide: Mechanistic and spectroscopic evidence for the effects of metal Lewis acidity and solvent Lewis basicity

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ARTICLE INFO

Article history:

Received 16 March 2018

Revised 4 June 2018

Accepted 8 June 2018

Keywords:

Oxidative desulfurization

Lewis acid catalysis

Zeolite catalysis

Solvent effects

Competitive adsorption

Mayr nucleophilicity

ABSTRACT

Group 4 (Ti and Zr) and 5 (Nb and Ta) atoms substituted into the β -BEA zeolite framework (M-BEA) irreversibly activate hydrogen peroxide (H_2O_2) and form pools of metal-hydroperoxide (M-OOH) and peroxide (M-($\eta^2\text{-O}_2$)) intermediates active for the oxidation of 2,5-dimethylthiophene ($\text{C}_6\text{H}_8\text{S}$), a model reactant representative of organosulfur species in fossil reserves and chemical weapons. Sequential oxidation pathways convert $\text{C}_6\text{H}_8\text{S}$ into 2,5-dimethylthiophene oxide ($\text{C}_6\text{H}_8\text{SO}$) and subsequently into 2,5-dimethylthiophene dioxide by oxidative dearomatization. Oxidation rates measured as functions of reactant concentrations together with in situ UV–vis spectra show that all M-BEA activate H_2O_2 to form pools of M-OOH and M-($\eta^2\text{-O}_2$), which then react with either $\text{C}_6\text{H}_8\text{S}$ or H_2O_2 to form the sulfoxide or to decompose into H_2O and O_2 , respectively. Turnover rates for $\text{C}_6\text{H}_8\text{S}$ oxidation and H_2O_2 decomposition both increase exponentially with the electron affinity of the active site, which is quantitatively probed via the adsorption enthalpy for deuterated acetonitrile to active sites. $\text{C}_6\text{H}_8\text{S}$ oxidation rates depend also on the nucleophilicity of the solvent used, and rates decrease in the order acetonitrile > *p*-dioxane \sim acetone > ethanol \sim methanol. In situ UV–vis spectra show that highly nucleophilic solvent molecules compete effectively for active sites, inhibit H_2O_2 activation and formation of reactive M-OOH and M-($\eta^2\text{-O}_2$) species, and give lower turnover rates. Consequently, this work shows that turnover rates for sulfoxidation are highest when highly electrophilic active sites (i.e., stronger Lewis acids) are paired with weakly nucleophilic solvents, which can guide the design of increasingly productive catalytic systems for sulfide oxidation.

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1. Introduction

Fossil fuel reserves and chemical warfare agent stockpiles contain potentially harmful organosulfur compounds (OSCs) that must be captured and sequestered by adsorption or deactivated by chemical or catalytic methods. These compounds threaten human and environmental health [1], because they are toxic in their native form but also because they form noxious species (i.e., SO_x) upon combustion. Crude fossil fuels contain up to 5 wt% OSCs [2], which must be reduced below 15 ppm (i.e., <0.015 wt%) to comply with environmental regulations for diesel fuels in many countries [3]. Furthermore, the sulfur contents of hydrocarbon feedstocks impact environmental pollution [4] but also the corrosion of equipment [5] and the reactivity of catalysts in down-stream processes [6]. OSCs are frequently removed from fossil fuels by

hydrodesulfurization (HDS), which reduces OSCs using molecular hydrogen to liberate hydrogen sulfide (H_2S) [7–10] that is captured by chemical separations (i.e., absorption) or treatment (to form elemental sulfur) [11]. Aromatic sulfur compounds (e.g., thiophenes) comprise the vast majority of OSCs within fossil fuel reserves [2]. Yet, many HDS catalysts (e.g., $\text{CoMo}/\text{Al}_2\text{O}_3$) give low rates for the hydrodesulfurization of hindered thiophenes (e.g., 4,6-dimethyldibenzothiophene) because the steric bulk surrounding the sulfide moiety hinders coordination to the catalyst surface [12,13]. Consequently, reduction of these compounds requires long residence times and harsh process conditions (e.g., high temperatures, high H_2 pressures) that leads also to undesirable hydrogenolysis reactions that reduce fuel quality [14,15].

Alternatively, oxidative desulfurization (ODS) can chemically abate the OSCs that are present in crude fuels without cleaving C–C bonds in long-chain hydrocarbons [16]. Oxidation of the sulfide moiety in thiophenes using environmentally benign oxidants, such as hydrogen peroxide (H_2O_2), produces less-toxic sulfoxide or

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sulfone products that are easily sequestered and analogous oxidations of many chemical warfare agents eliminates their bioactivity [17]. Multiple articles have reported the synthesis and evaluation of titanium silicalite (TS-1) [16,18–21], titania-silicates (TiO₂-SiO₂) [22–24], Ti-BEA [21,25–27], and other Ti-based catalysts [28,29] for the oxidation of thiophenes. For example, Corma and coworkers have shown that Ti-BEA and Ti-MCM-41 are both active for the oxidation of methylphenyl sulfide (0.1 M, 0.3 M H₂O₂, CH₃CN solvent, 313 K) [21], with Ti-BEA possessing greater rates for sulfoxidation than Ti-MCM-41. When methylphenyl sulfide was exchanged for isopentylmethyl sulfide Ti-MCM-41 possessed greater rates, which was attributed to slower diffusion through the smaller-pore Ti-BEA. Hulea et al. have shown that Ti-BEA and Ti-HMS (HMS = hexagonal mesoporous silica) catalyze the oxidation of benzothiophene and dibenzothiophene, both of which were shown to be too bulky to enter the pores of MFI and react with TS-1 [25]. Notably, Ti-BEA was shown to possess higher rates than Ti-HMS, which we presume to be related to stabilization of the bulky thiophenic transition states within the smaller-pore BEA. Thornburg et al. have recently shown that niobium silicates (Nb-SiO₂) efficiently oxidize thioanisole and possess nearly perfect selectivity toward the formation of the corresponding sulfone [28]. The Nb-SiO₂ catalysts are also significantly more active for thioanisole oxidation than Ti- and Zr-SiO₂ at 318 K, which exhibit initial turnover rates of 9.0, 7.9, and 2.3 min⁻¹, respectively [24]. These trends differ markedly different from those for epoxidation catalysis on similar materials, where rates of cyclohexene and styrene epoxidation are greatest for Ti-incorporated BEA and Ti-SiO₂, followed by the Nb analogues [30–33]. Currently, the reasons for the differences in thiophene oxidation rates and selectivities are unknown but may be related to changes in the mechanism for oxidation or to differences in the electronic structure and coordination of the active sites. Overall, the literature lacks a detailed mechanism for the oxidation of substituted thiophenes or guiding principles for the design of improved groups 4 and 5 catalytic systems for sulfoxidation chemistry.

Here, we seek to explain how and why rates and selectivities for the oxidation of 2,5-dimethylthiophene (C₆H₈S) depend on the intrinsic properties of active sites formed by substituting group 4 or 5 transition metal atoms into the framework of zeolite BEA (M-BEA). A combination of reaction rates measured as a function of the reactant concentrations, in conjunction with spectroscopic measurements acquired in situ, show that all M-BEA activate H₂O₂ and oxidize C₆H₈S through a series of equivalent elementary steps that utilize similar reactive species. Comparisons of turnover rates for C₆H₈S oxidation within different solvents show that conversion rates depend exponentially on the nucleophilicity of the solvent mixture, which is quantified using the Mayr nucleophilicity scale. UV-vis spectra of Ti-BEA contacted by H₂O₂ solutions in these different solvent mixtures show a concomitant decrease in the number of M-(O₂) intermediates and C₆H₈S oxidation rates, which suggests that competitive adsorption of these Lewis basic solvents to the Lewis acidic metal centers contributes to the decrease in rates. These comparisons show that thiophene oxidation depends sensitively on the Lewis acid-base interactions between the active sites and the solvent molecules. Finally, reaction rates for C₆H₈S oxidation and H₂O₂ decomposition increase with a similar functional dependence on the electron affinity of the active sites, which are quantitatively compared using the adsorption enthalpy of deuterated acetonitrile to Lewis acid sites. Consequently, the design of catalytic systems that maximize the electron affinity of the group 4 or 5 metal center and utilize weakly Lewis basic solvent system give greater turnover rates for ODS without sacrificing the selective use of the costly oxidant, H₂O₂.

2. Methods and materials characterization

2.1. Synthesis and characterization of M-BEA

Ti-, Nb-, and Ta-BEA catalysts were synthesized by the post-synthetic modification of NH₄⁺-BEA, while Zr-BEA was prepared by solid-state ion exchange of NH₄⁺-BEA [30,31,34–37] and is detailed in our previous reports [30–32]. In short, NH₄⁺-BEA (Zeolyst, CP814E) was dealuminated by reflux in HNO₃ (20 mL g⁻¹; Macron Chemicals, 69–70%) to produce Si-BEA (Si:Al > 1400, determined by EDXRF). Ti-, Nb-, and Ta-BEA were synthesized by refluxing an appropriate amount of Si-BEA with the corresponding metal chloride (TiCl₄ (Sigma, 99%), NbCl₅ (Sigma, 99.9%), TaCl₅ (Sigma, 99%)) in either dichloromethane (for Ti) or isopropanol (for Nb and Ta; Fisher Chemicals). Solids were then recovered by rotary evaporation. Zr-BEA was produced by grinding Si-BEA with an appropriate amount of Zr(OEt)₄ (Alfa-Aesar, 99%) to form an intimate mixture. In all cases, recovered solids were treated in flowing air (100 cm³ min⁻¹; Airgas, Ultra-zero grade) and were heated to 823 K at 2 K min⁻¹ for 6 h, which produced bright white solids.

The metal contents (Table 1) of the M-BEA catalysts were quantified using energy dispersive X-ray fluorescence (EDXRF) spectroscopy. Briefly, 30–40 mg of sample was loaded into a polypropylene sample holder (1 cm diameter) that was sealed with ultralene film. These were then loaded into a spectrometer (Shimadzu, EDX-7000), whose sample chamber compartment was purged with He. One hundred scans were taken from 0 to 30 keV and the relative intensities of the fluorescence features for each element was used to determine the percent by mass of each element present.

The crystallinity of the M-BEA materials and differences in framework bond lengths before and after post-synthetic modification were determined using powder X-ray diffraction. Samples were finely ground and loaded (~60 mg) onto a polycarbonate holder, which was mounted into a diffractometer (Siemens/Bruker, D5000) with Cu K α radiation (0.15418 nm). All X-ray diffractograms (Fig. S1) were collected under ambient conditions. X-ray diffractograms were smoothed using a finite Fourier transform with 10 points of fitting and the highest intensity was used to determine the positions of peak centers.

Optical band edge energies (E_g) were determined by extrapolation of the linear portion of the corresponding Tauc plot calculated from diffuse reflectance UV-vis spectra (Fig. S2). M-BEA samples were intimately combined in a 1:10 by weight ratio with magnesium oxide (MgO; Sigma, 99.995%) prior to analysis. Total reflectance spectra were collected at ambient conditions on a UV-vis-NIR spectrophotometer (Agilent, CARY 5) using pure MgO as a background.

The heat of adsorption for deuterated acetonitrile (CD₃CN; Cambridge Isotopes, 99.8% D atom) bound to the cationic framework transition metal atoms (ΔH_{CD_3CN}) is used as a quantitative measure

Table 1

Band edge energies, silicon-to-metal ratios, metal loadings, silicon-to-aluminum ratios, and heats of adsorption for CD₃CN coordinated to Lewis acidic metal atoms for M-BEA catalysts used for catalytic rate measurements.

Sample	Band edge (eV) ^a	Si:M ratio ^b	Weight loading (wt. %)	Si:Al ratio ^b	ΔH_{CD_3CN} (kJ mol ⁻¹) ^c
Ti-BEA	4.2	550	0.14	>1400	-31 ± 2
Zr-BEA	5.3	60	2.4	>1400	-12 ± 1
Nb-BEA	4.0	690	0.22	>1400	-20 ± 2
Ta-BEA	4.6	570	0.53	>1400	-16 ± 2

^a Measured by diffuse reflectance UV-vis spectroscopy.

^b Measured by energy dispersive X-ray fluorescence spectroscopy.

^c Determined using van't Hoff analysis of infrared spectra.

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