

## Acid Site effects on the photocatalytic properties of ETS-10 & ETVS-10s toward the reduction of VOCs

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### Introduction

We have investigated ETS-10 and vanadium-incorporated ETS-10 as photocatalysts for the reduction of volatile organic components (VOCs) since their unique structure may help elucidate the material and surface properties needed to overcome some of the disadvantages of traditional semiconductors like anatase. ETS-10 is a microporous titanosilicate<sup>1</sup> composed of octahedral chains of TiO<sub>6</sub> embedded in a tetrahedral SiO<sub>4</sub> framework. These chains stack perpendicular to each other to form a 7.5 Å, three-dimensional channel structure with an ideal stoichiometry of (Na, K)<sub>2</sub>TiSi<sub>5</sub>O<sub>13</sub>. Vanadium has been shown to substitute for the titanium along the chain forming (V/(V+Ti))ETVS-10s and can completely replace titanium forming an analogous structure to ETS-10, called AM-6.<sup>2,3</sup> This incorporation of vanadium has also shown visible photocatalytic activity that has been explained experimentally and theoretically.<sup>4,5</sup>

These chains of TiO<sub>2</sub> behave as 1D semi-conducting wires which are insulated by the SiO<sub>2</sub> framework. Therefore chain termination sites on the surface of the crystal or at defects along the chain play a crucial role in the electron-hole transfer from the chain to adsorbed organic molecules. Previous work has shown that ion exchange leads to an increase in chain termination for ETS-10 samples along with different photocatalytic properties.<sup>6,7</sup> In this research we will determine the effects of acid site formation through NH<sub>4</sub> ion exchange in an attempt to maximize the photocatalytic reactivity of the ETVS-10 samples for VOCs decomposition.

### Materials and Methods

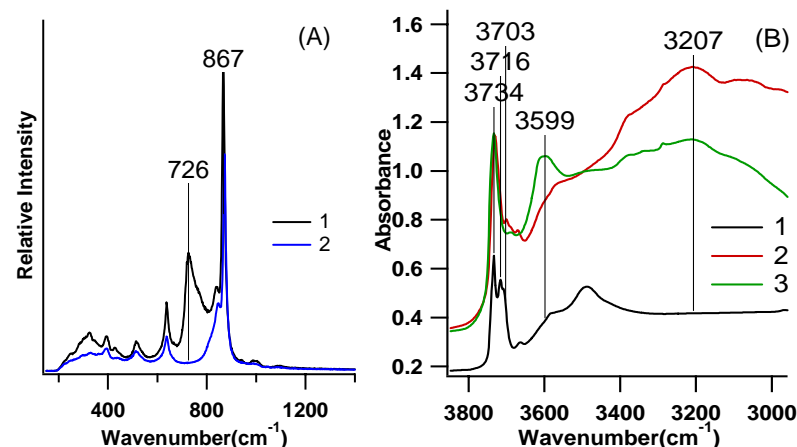
Materials were characterized using X-ray diffraction (XRD), N<sub>2</sub> adsorption, scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), UV/vis spectroscopy, and Raman spectroscopy.

A Diffuse Reflectance Infrared Fourier Transform Spectrometer (DRIFTS) coupled with a UV-lamp has been implemented to investigate the formation of electron-hole pairs upon excitation of ETS-10 and ETVS-10s. In-situ illumination and pulsed flow of oxidants and reducing agents will be used to investigate the intermediates and products formed during the photocatalytic reaction.

### Results and Discussion

The NH<sub>4</sub> ion exchange has shown to cause a coordination change (Figure 1A) for Ti with the loss of the Ti-O-Ti chain stretch at 726 cm<sup>-1</sup>. However, the same effect was not observed for the analogous V-O-V stretch at 867 cm<sup>-1</sup>. The ion exchange also created acid sites (Figure 1B)

at 3599 cm<sup>-1</sup> upon thermal breakdown of the NH<sub>4</sub> ion (3207 cm<sup>-1</sup>) for the Ti containing samples, giving different active sites for reaction compared to the untreated samples with just the characteristic Si-OH, Ti-OH, and V-OH (3734, 3716, 3703 cm<sup>-1</sup>) surface sites. These differences in structural properties have lead to a large difference in the photocatalytic reactivity of these materials. In which, the Ti exchanged samples show total oxidation of VOCs and the all vanadium samples only achieve partial oxidation.



**Figure 1.** (A) Raman spectra of 1-Untreated 0.43ETVS-10 and 2-NH<sub>4</sub> exchanged 0.43ETVS-10. (B) FTIR spectra of 1-Untreated 0.13ETVS-10, 2-NH<sub>4</sub> exchanged 0.13ETVS-10 at 100°C for 2 hrs, and 3-NH<sub>4</sub> exchanged 0.13ETVS-10 at room temperature after 24 hrs of being heated at 350°C.

### Significance

This research suggests that there is an optimal vanadium concentration that lowers the band gap while still allowing for the total oxidation of VOCs in the ETVS-10 structures.

### References

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