Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


**Supporting Information**

# Heteroatom Substituted Zeolite FAU with Ultralow Al Contents for Liquid-Phase Oxidation Catalysis

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## S1.0 Characterization of Ti-BEA, Ti-$SiO_2$, and TS-1

### S1.1 X-ray Diffraction of Ti-BEA and TS-1

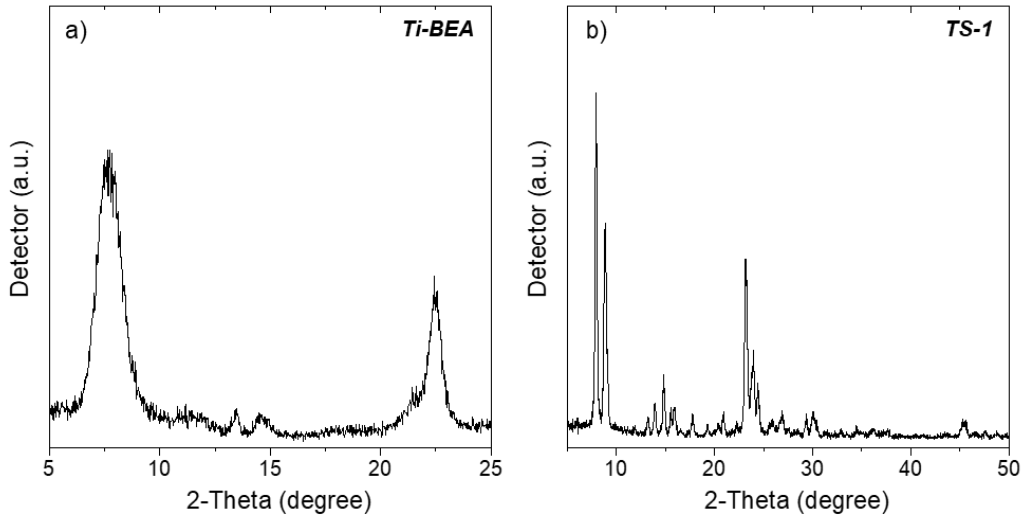


**Figure S1.** X-ray diffractograms of (a) Ti-BEA and (b) TS-1.

Figure S1 shows X-ray diffractograms for Ti-BEA and TS-1, which indicate that these materials contain diffraction features characteristic of the BEA and MFI zeolite frameworks, respectively.

**S1.2 Diffuse Reflectance UV-vis of Ti-BEA, Ti-$SiO_2$, and TS-1**

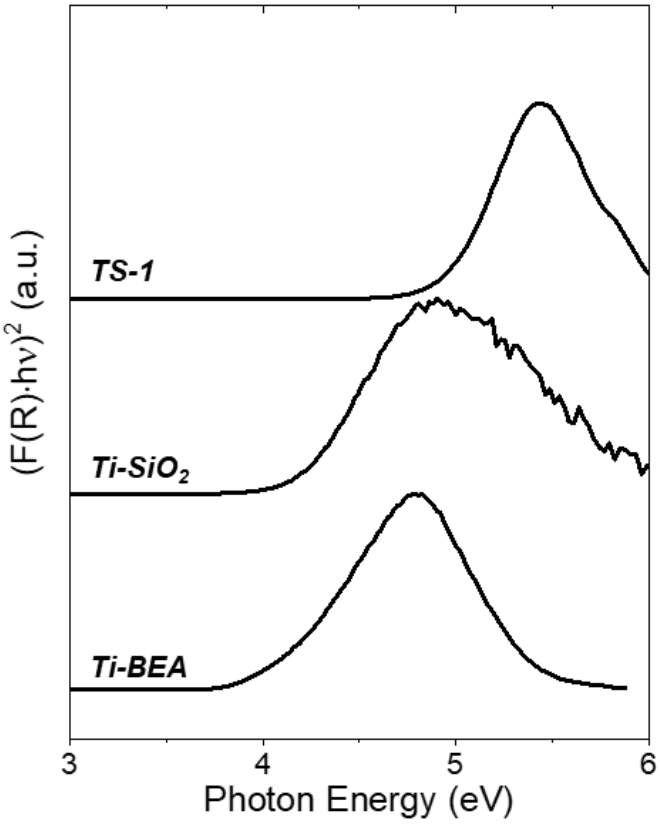


**Figure S2.** Tauc plots for Ti-BEA, Ti-$SiO_2$, and TS-1. Note that F(R) corresponds to the Kubelka-Munk pseudo-absorbance. All spectra were normalized to the most-intense feature and are vertically offset for clarity.

## S2.0 M-FAU Characterization

### S2.1 X-Ray Diffraction to Show Changes in Lattice Spacing

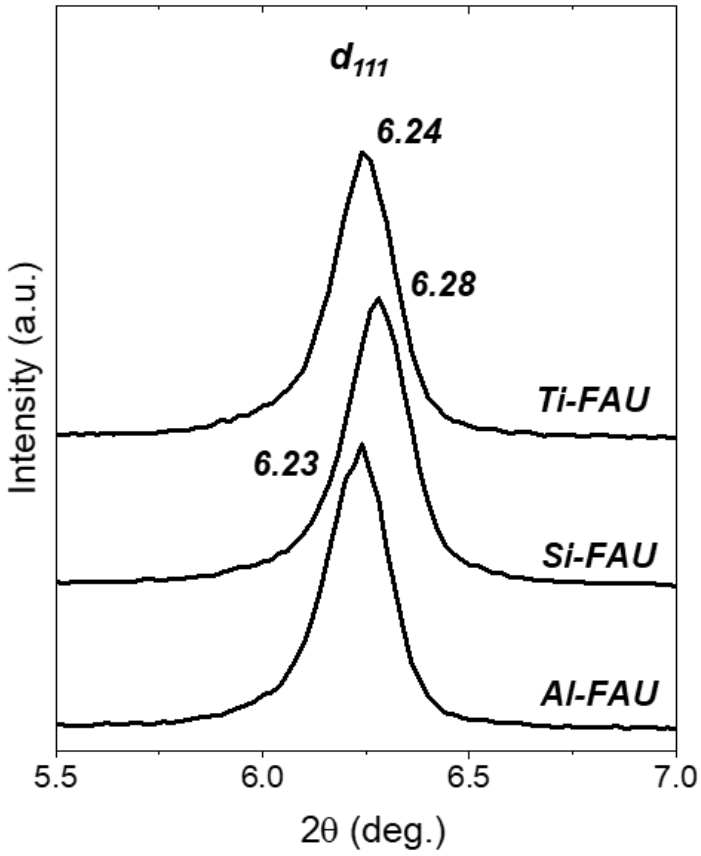


**Figure S3.** X-ray diffractograms for Al-, Si-, and Ti-FAU. Diffractograms are vertically offset for clarity.

**S2.2 Nitrogen Volumetric Adsorption to Show Isotherm Type**

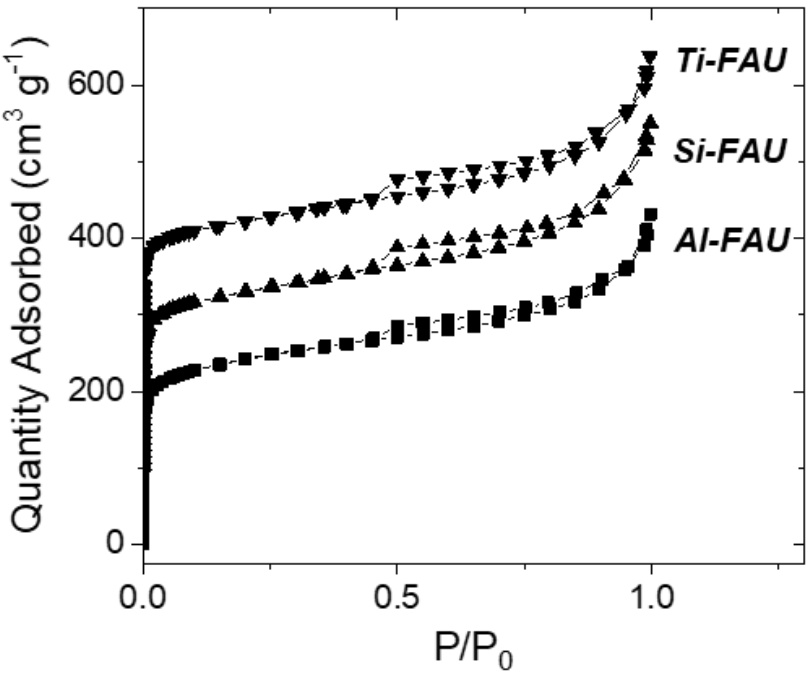


**Figure S4.** Nitrogen adsorption isotherms (77 K) for Al-, Si-, and Ti-FAU. Adsorption isotherms are offset for clarity.

## S2.3 $^{29}$Si MAS-NMR Spectra to Visualize $Q^4$ Features

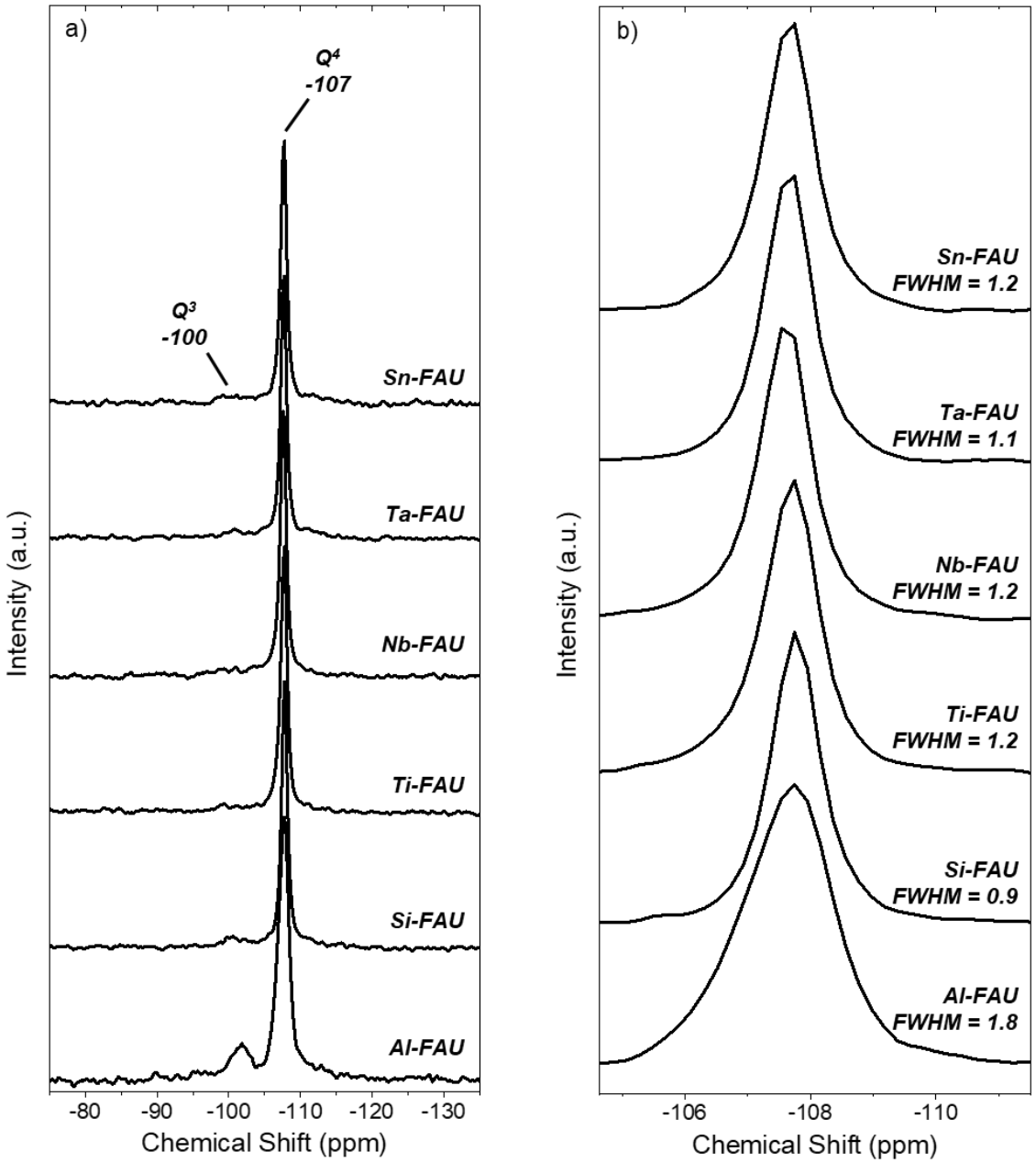


**Figure S5.** (a) $^{29}$Si direct polarization MAS-NMR spectra of Al-, Si-, Ti-, Nb-, Ta-, and Sn-FAU. Panel (b) shows changes in the full width-half max (FWHM) of the $Q^4$ features within each M-FAU. All spectra are normalized to the $Q^4$ feature and are offset for clarity.

## S3.0 Peak Fitting Procedures

### S3.1 $^{29}$Si MAS-NMR of Si-FAU Example Peak Fitting

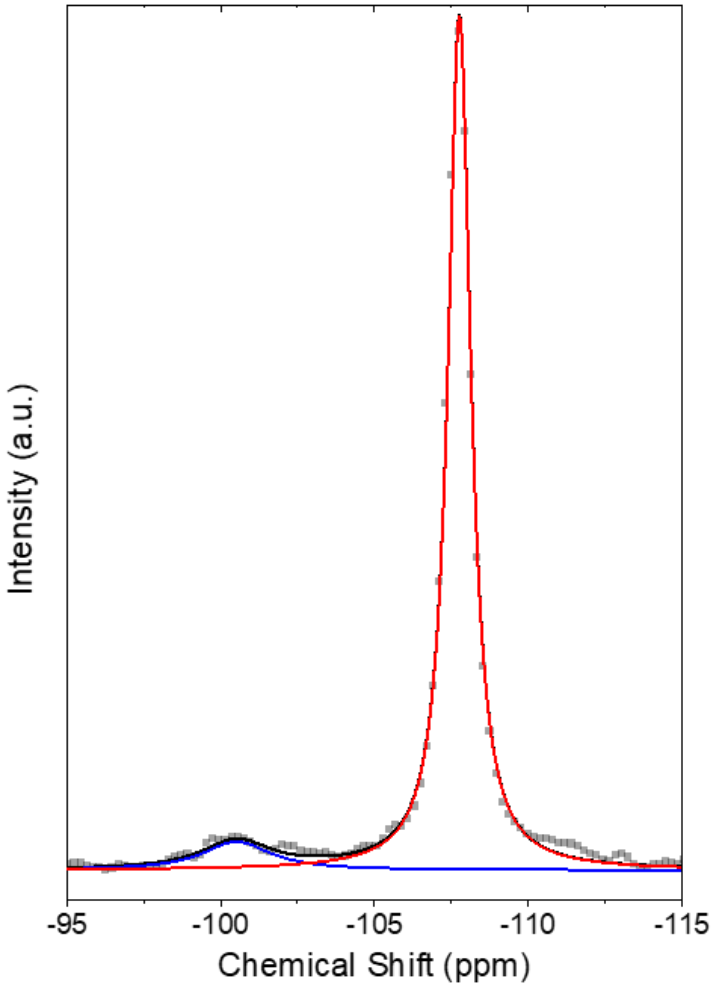


**Figure S6.** Example peak fitting procedure for $^{29}$Si MAS-NMR spectra (gray ■) of Si-FAU. The red curve represents NMR features attributed to $Q^4$ sites, while the blue curve represents those belonging to $Q^3$ sites; the black curve is the cumulative fit. In all cases, Lorentzian curves were used for the fitting procedure. Values of $\phi_{NMR}$ were estimated by dividing the area under the blue curve to that of the black curve.

**S3.2 Infrared Spectroscopy of Dehydrated Si-FAU Example Peak Fitting**

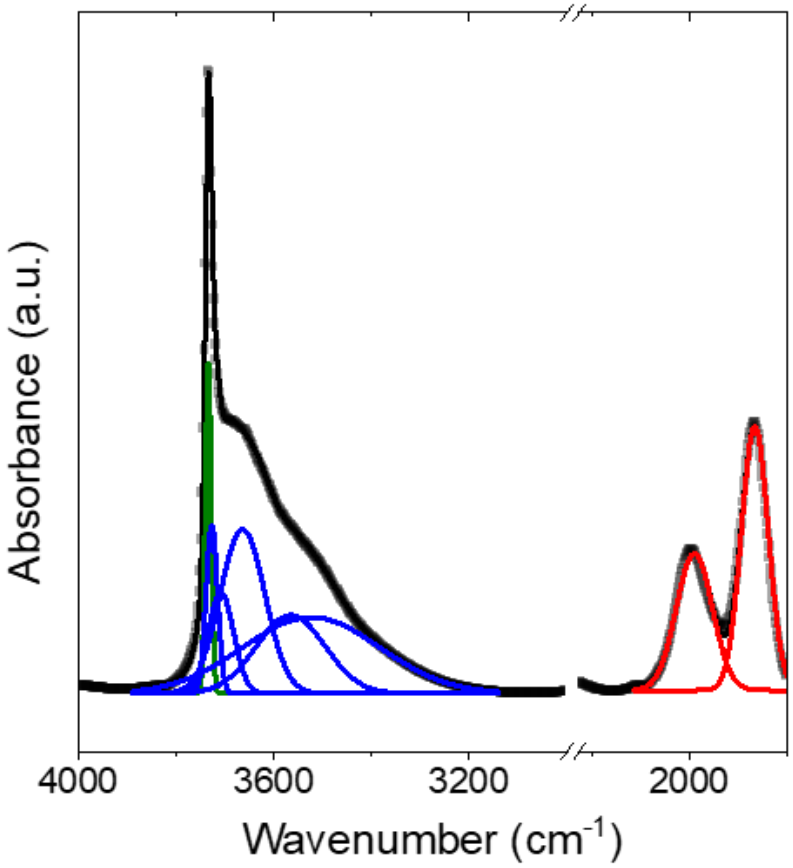


**Figure S7.** Infrared spectra (gray ■) of dehydrated Si-FAU (573 K, He). Gaussian curves were used to fit the data in all cases. The green curve represents ν(O-H) of isolated SiOH, the blue curves are ν(O-H) resulting from hydrogen-bonded SiOH (e.g., $(SiOH)_4$), and red curves represent ν(Si-O-Si) overtone stretches. The black curves represent cumulative fits.

Six gaussian curves were chosen to fit the infrared spectra of M-FAU in order to capture the proper curvature and yield a $R^2$ value >0.995. Fitting procedures using three-to-five gaussian curves yielded nearly identical values of $\phi_{IR}$.

**S4.0 Epoxidation of 2,4-dimethylstyrene**

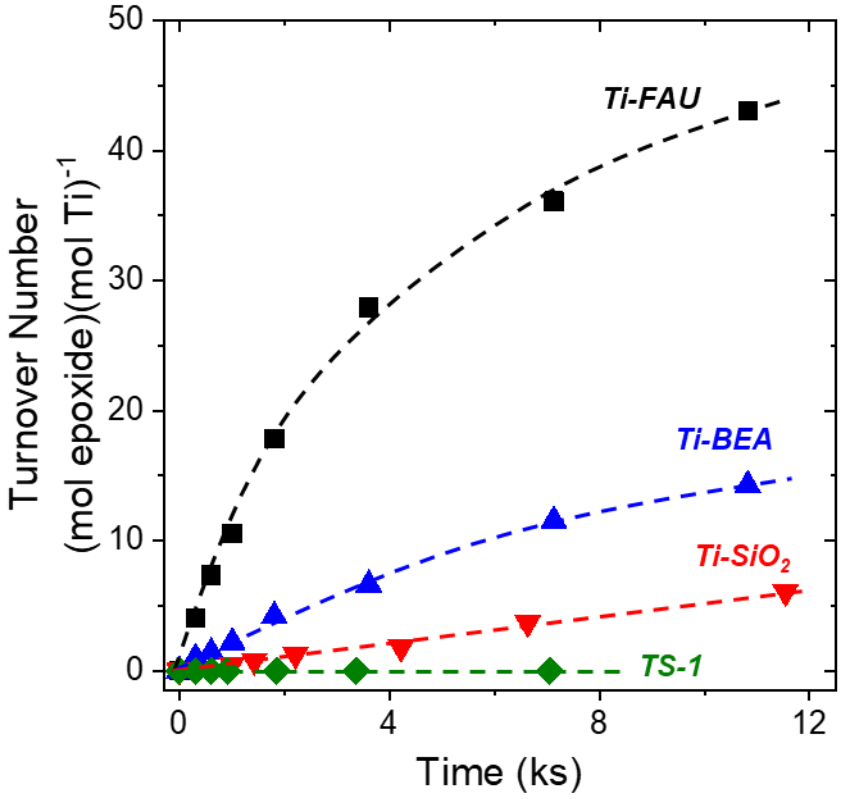


**Figure S8.** Turnover numbers as a function of time for the epoxidation of 2,4-dimethylstyrene (0.1 M 2,4-dimethylstyrene, 0.1 M $H_2O_2$, in $CH_3CN$, 313 K) over Ti-FAU (black ■), Ti-BEA (blue ▲), Ti-$SiO_2$ (red ▼), and TS-1 (green ♦). Dashed curves are intended to guide the eye.

Figure S8 shows the turnover numbers for 2,4-dimethylstyrene epoxidation over Ti-FAU, Ti-BEA, Ti-$SiO_2$, and TS-1. Turnover numbers (and rates) for 2,4-dimethylstyrene epoxidation are greatest within Ti-FAU and decrease in the order Ti-BEA, Ti-$SiO_2$, and TS-1. Notably, rates of 2,4-dimethylstyrene epoxidation are immeasurable on TS-1 because TS-1 possesses pores that are 0.55 nm in diameter, which is smaller than the kinetic diameter of 2,4-dimethylstyrene (e.g., *m*-xylene has a kinetic diameter of 0.68 nm),[1] which precludes the diffusion and reaction of 2,4-dimethylstyrene within the MFI framework. The increased turnover numbers for 2,4-dimethylstyrene oxide formation within Ti-FAU relates to the increased entropic freedom of the transition state for epoxidation within Ti-FAU compared to Ti-BEA, with the increased enthalpic stabilization relative to Ti-$SiO_2$.

## References:

1. M. Jahandar Lashaki, M. Fayaz, S. Niknaddaf and Z. Hashisho, *J. Hazard. Mater.*, 2012, **241-242**, 154-163.