Supplementary Materials: Acidity-Reactivity Relationships in Catalytic Esterification over Ammonium Sulfate-Derived Sulfated Zirconia

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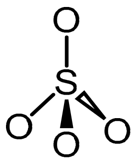
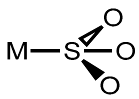
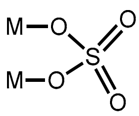
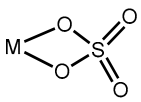
2. Results and Discussion

2.1. Catalyst Characterization

Table S1. Sulfate configuration and associated vibrational frequencies of IR active modes from [1].

Structure	Symmetry	v_1	v_2	v_3	v_4
 **Free $(SO_4)^{2-}$**	T_d	—	—	1104 (vs)	613 (s)
 **Unidentate**	C_{3v}	970 (m)	438 (m)	1032–1044 1117–1143	645 (s) 664 (s)
 **Bridging bidentate**	C_{2v}	995 (m)	462 (m)	1050–1060 (s) 1170–1105 (s)	641 (s) 610 (s) 571 (m)
 **Chelating bidentate**	C_{2v}	—	—	1211, 1175, 1176	—

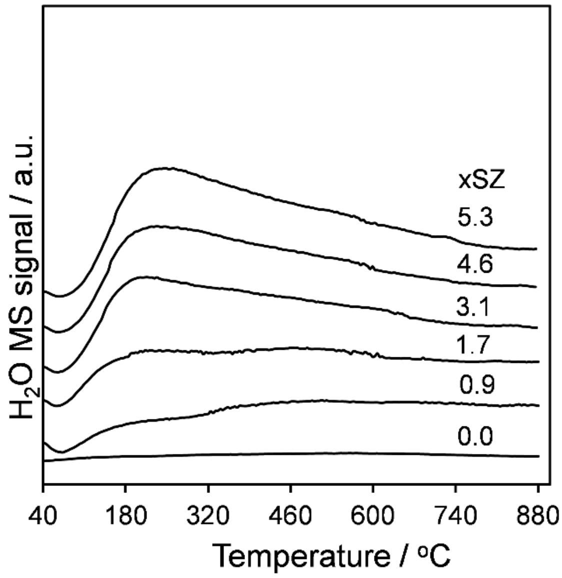


Figure S1. Evolved H_2O (m/z=18 amu) during thermal analysis of parent and sulfated zirconia as a function of bulk S loading.

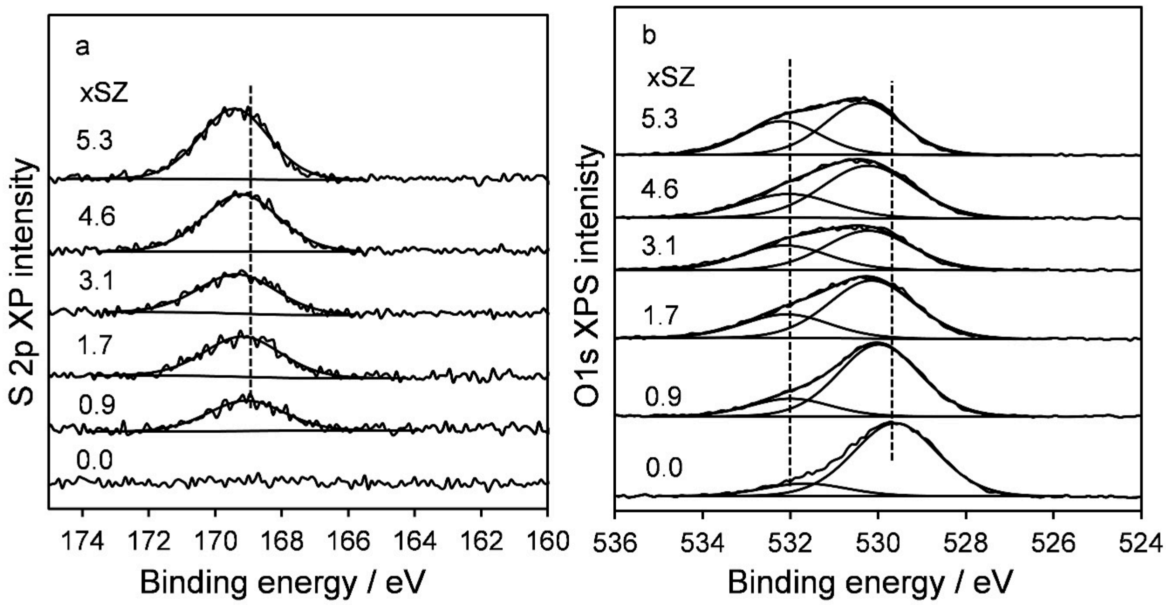


Figure S2. (**a**) S 2p and (**b**) O 1s XP spectra for parent and sulfated zirconia as a function of bulk S loading.

2.2. Surface Acidity

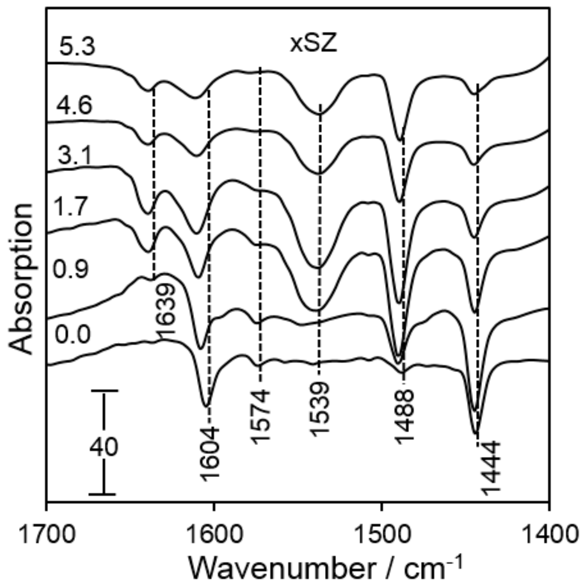


Figure S3. In situ IR νCCN spectra of irreversibly adsorbed pyridine at 100 °C on parent and sulfated zirconia as a function of bulk S loading.

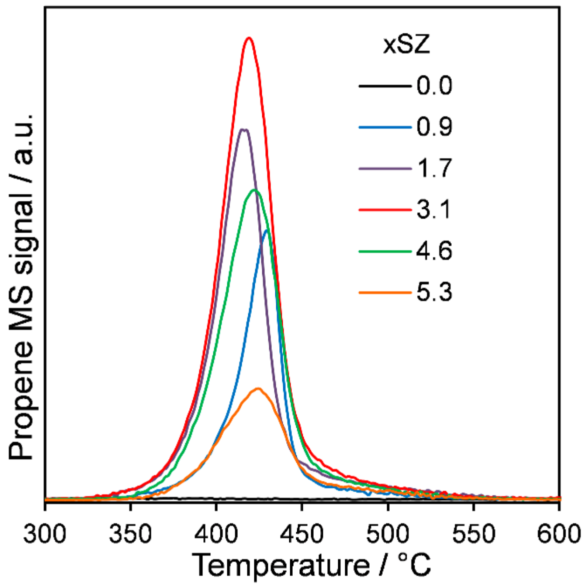


Figure S4. TPD profiles of adsorbed n-propylamine monitoring the release of reactively formed propene on parent and sulfated zirconia as a function of bulk S loading.

2.2.1. Methylbutynol Decomposition

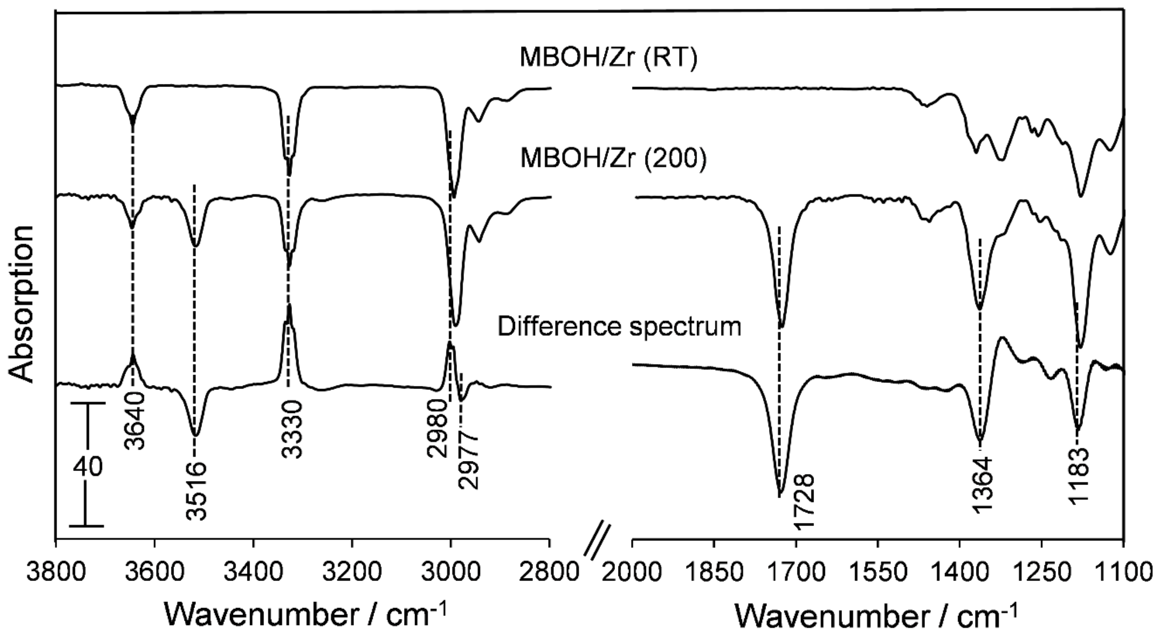


Figure S5. Difference IR gas phase spectra following MBOH(g) adsorption over the parent zirconia before and after heating at 200 °C for 5 min.

2.3. Catalytic Esterification of Propanoic Acid

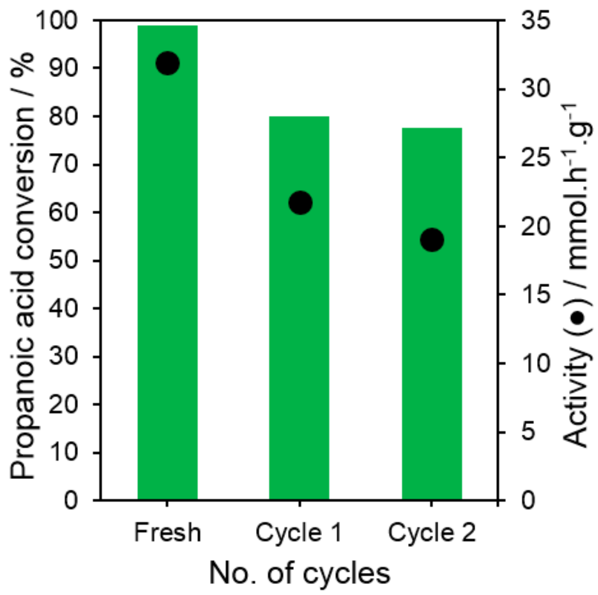


Figure S6. Propanoic acid conversion and mass-normalized rates of esterification of a fresh and recycled 1.7 wt % SZ catalyst.

Reference

G. Lefèvre, In-situ Fourier-transform infrared spectroscopy studies of inorganic ions adsorption on metal oxides and hydroxides. *Adv. Colloid Interface Sci.* **2004**, *107*, 109–123.