Supplemental Information for

Site and Structural Requirements for the Dehydra-decyclization of Cyclic Ethers on ZrO_2

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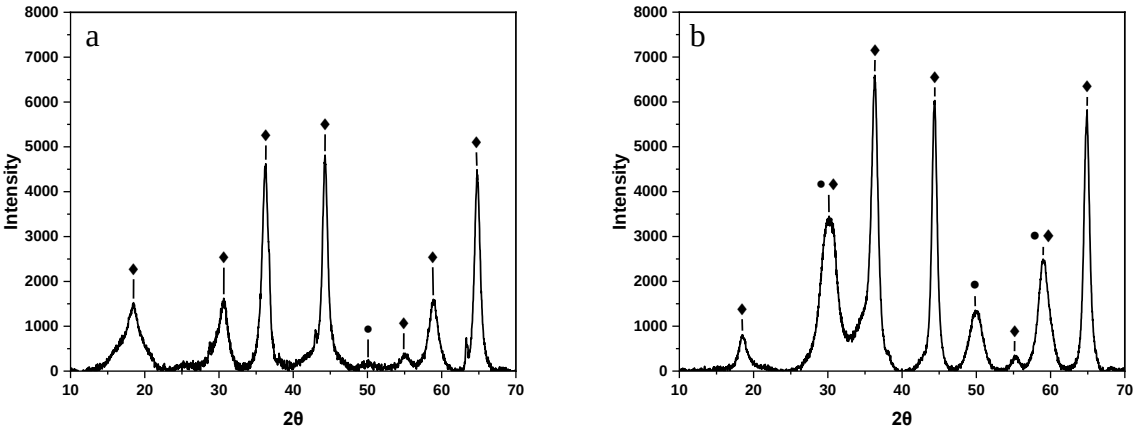

Figure S1. XRD pattern of a) 0.5 nm ZrO_2 on MAO; b) 1nm ZrO_2 on MAO. • for tetragonal ZrO_2 and ◆ for MAO.

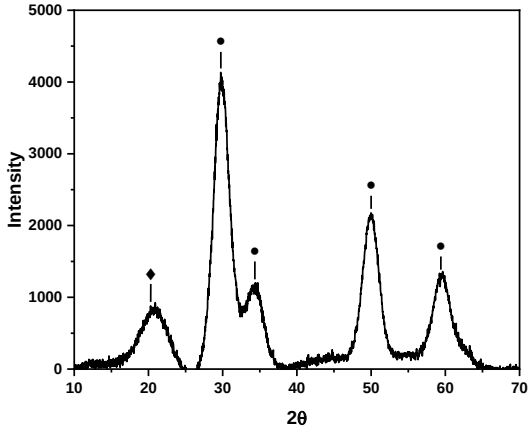

Figure S2. XRD pattern of 1nm ZrO_2 on SiO_2. • for tetragonal ZrO_2 and ◆ for SiO_2.

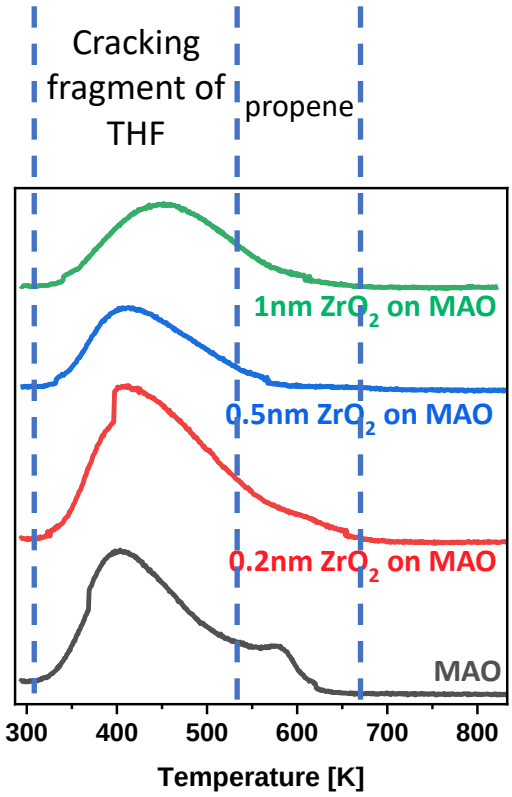

Figure S3. Propene TPD peak (m/e 42 at high temperature) from THF-dosed samples as a function of the ZrO_2 film thickness. m/e 42 was used here for propene rather than m/e 41 which is also in the cracking pattern for butadiene.

FTIR Analysis

Fourier transform infrared (FTIR) spectroscopy of pyridine dosed ZrO_2 as a function of the Na loading was used to characterize surface Lewis and Brønsted acid sites. These spectra were collected using a Bruker Tensor II spectrometer equipped with a DLaTGS detector and mid-IR source. Spectra were recorded between 1000 and 6000 cm^{-1} with a 4 cm^{-1} resolution, averaged over 64 scans and subtracted from a background spectrum. Thin self-supporting catalyst wafers were prepared by pressing 10−15 mg of finely ground ZrO_2 powder into a pellet which was then transferred into a custom-built heated transmission cell. The catalyst wafer was first annealed in-situ (60 sccm He 99.999 %) at 373 K for 10 mins using a ramp rate of 3 K min−1, after which it was cooled down to room temperature to take an IR spectrum of the parent catalyst. 10 torr of pyridine was fed to a vaporization section through a 1/16″ PEEK capillary line (0.01″ I.D., TPK110, Vici Valco) using a syringe pump (Masterflex EW-74905-04, Cole-Parmer) and air-tight glass syringes (Hamilton Company, model number), constantly swept by a stream of He (99.999%, Airgas), the flow of which was adjusted using mass flow controllers (Type 201, Porter). The samples were exposed to 10 torr of pyridine for 10 minutes, physisorbed pyridine was removed by flushing with 60 sccm of He for 60 minutes, after which spectra were recorded.

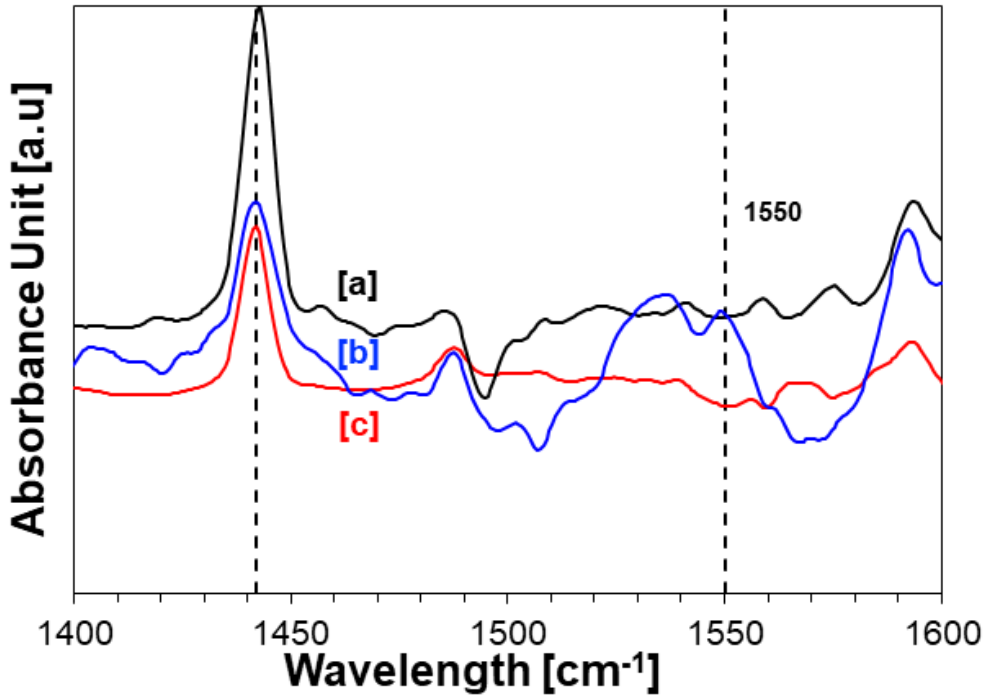

Figure S4. FTIR spectra of pyridine-dosed **[a]** bulk ZrO_2, **[b]** 1 wt % Na-ZrO_2, and **[c]** 2 wt % Na-ZrO_2.

Note that the spectra for all three samples show a prominent band at 1442 cm^{-1} which is characteristic of pyridine adsorbed on Lewis acid sites (*i.e.* Zr^{4+} sites). A peak near 1150 cm^{-1} is characteristic of pyridine adsorbed on a Brønsted acid sites (adsorbed pyridinium ion). While there is some inconsistency in the data in this region, especially for the 1 wt % Na sample, no peaks in this region are observed for the ZrO_2 and 2 wt % Na-ZrO_2 samples. These results suggest that the Na covered samples retain their Lewis acid site functionality, while not incurring any additional Brønsted acid site functionality due to the Na cations.

TPD Analysis

Mass spectrometer sensitivity factors for the individual products were used to quantify the TPD data which were calculated using the procedure that is described in E. I. Ko, J. B. Benziger, and R. J. Madix, *J. Catal.* **62**, 264–274 (1980).

Verification that reactivity data was collected under reaction-limited conditions

The Thiele modulus is the ratio of the reaction rate to that of the diffusion rate. A Thiele modulus of less than one is required to ensure that rate data is collected under conditions where the rate is reaction limited rather than diffusion limited.

The following parameters were used to estimate the Thiele modulus:

Diffusivity of THF: D = 1 x 10^{-5} m^2/sec (typical value for gasses)
Characteristic length: L = 1 x 10^{-3} m (characteristic length scale of our pelletized catalysts)
Flow rate of THF: F_{THF} = 200 ml/hr = 0.056 ml/sec
Density: ρ = 0.889 g/mlWeight of catalyst: m = 0.1 g
Conversion for calculation: X = 0.5
Calculated rate constant: $k = \frac{F_{THF} \cdot X \cdot \rho}{m} = 0.02\ s^{-1}$ (assuming first order kinetics)

Thiele modulus $\phi_1 = L\sqrt{\frac{k}{D}} = 0.44$

Since the Thiele modulus is less than one diffusion should not be rate limiting.

It should also be noted that even if some mass transfer limitations were present, it would not change the interpretation of the data. Note that we do not make a comparison of the overall activity of the different types of samples that were studied (*i.e.* bulk powder, thin films, single crystals); instead, it is the change in reactivity for a given type of catalyst as a specific parameter, such as Na coverage, film thickness, etc., is varied which provides insight. Even if mass transfer limitations were present it would not vary as these parameters are varied, so it is not a relevant consideration.