Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Beyond Ketonization: Selective Conversion of Carboxylic Acids to Olefins over Balanced Lewis Acid-base Pairs

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Materials and Methods:

Catalysts synthesis

The $Zn_xZr_yO_z$ mixed oxides were synthesized via incipient wetness impregnation of a $Zn(NO_3)_2$ solution on $Zr(OH)_4$. The $Zr(OH)_4$ was initially dried overnight at 100 °C before impregnation. After impregnation, the catalysts were dried overnight at room temperature followed by 4 hours at 105 C prior to calcination. The catalyst were then calcined via a 3 °C/min ramp to 400 C which was held for 2 hours followed by a 5 °C/min ramp to the final calcination temperature (usually 550 °C) which was then held for 3 hours. The concentration of $Zn(NO_3)_2$ solution was varied to control the Zn/Zr ratio.

Catalyst characterization

Diffusion Reflectance Infrared Fourier Spectra analysis of adsorbed pyridine (IR-Py) were recorded on a Bruker Tensor 27 FTIR spectrometer. Experimental details have been reported elsewhere.[1] For the co-adsorbed H_2O experiment, pyridine was first adsorbed the same way as the IR-Py experiment. The sample was then ramped to 250 °C for 30min of desorption of pyridine, where water is then introduced while IR was used to monitor the surface of the catalyst.

Nitrogen sorption experiments were carried out at liquid nitrogen temperatures (-196 °C) on the Micromeretics TriStar II 3020 physisorption analyzer. Prior to measurement, samples were degassed at 350 °C for 3 h under vacuum.

Catalytic reactions

The catalysts were evaluated in a home-built test unit described elsewhere *(13)*. Briefly, a given amount of catalyst was loaded into a tubular fixed-bed reactor (i.d., 5 mm) and pretreated at 450 °C with 50 SCCM N_2 for 30 minutes. A reactant/water solution with steam-to-carbon molar ratio (S/C) of 5 is typically used unless otherwise stated. The solution was vaporized at in an evaporator at 150 °C and carried into the reactor by flowing N_2. Products were analyzed online using a Shimadzu GC-2014 Gas Chromatography (GC) equipped with HP-Plot Q column (30 m, 0.53 mm, 40 µm), flame ionization detector (FID), and thermal conductivity detector. Equations 1-3 show the ideal reaction for ethanol to isobutene, acetone to isobutene, and acetic acid to isobutene reactions. Based on the equations, the theoretical carbon selectivity to isobutene (S_{t-IB}) for ethanol to isobutene, acetone to isobutene, and acetic acid to isobutene are 66.7%, 88.9% and 66.7%, respectively. Conversion (X_r), products carbon selectivity ($S_{product-i}$), and isobutene theoretical yield (Y_{t-IB}) were calculated as follows: $X_r = (Mol_{reactant-in} - Mol_{reactant-out})/(Mol_{reactant-in})$; $S_{product-i} = \sum(Mol_{product-i} \times \alpha_i)/(Mol_{reactant} \times \beta)$, α_i and β refers to the carbon number in product-i and reactant, respectively; $Y_{t-IB} = X_{IB}/S_{t-IB}$.

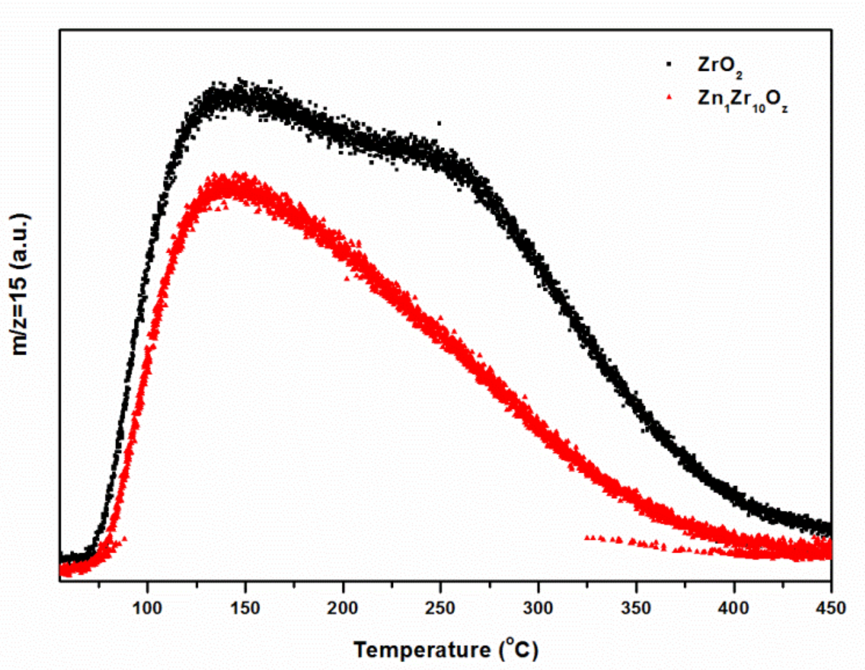


Figure S1. NH_3-TPD on the ZrO_2 and $Zn_1Zr_{10}O_z$.The addition of ZnO passivated the strong acidic sites on ZrO_2.

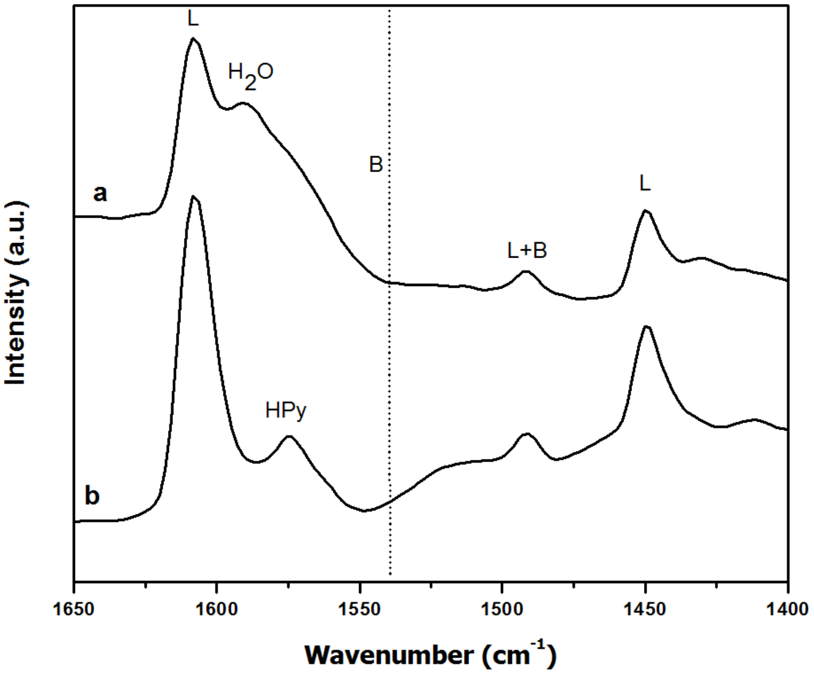


Figure S2. IR-Py of $Zn_1Zr_{10}O_z$ with (a) and without co-adsorbed H_2O (b) at a desorption temperature of 250 ºC. Note: No Brønsted acid sites

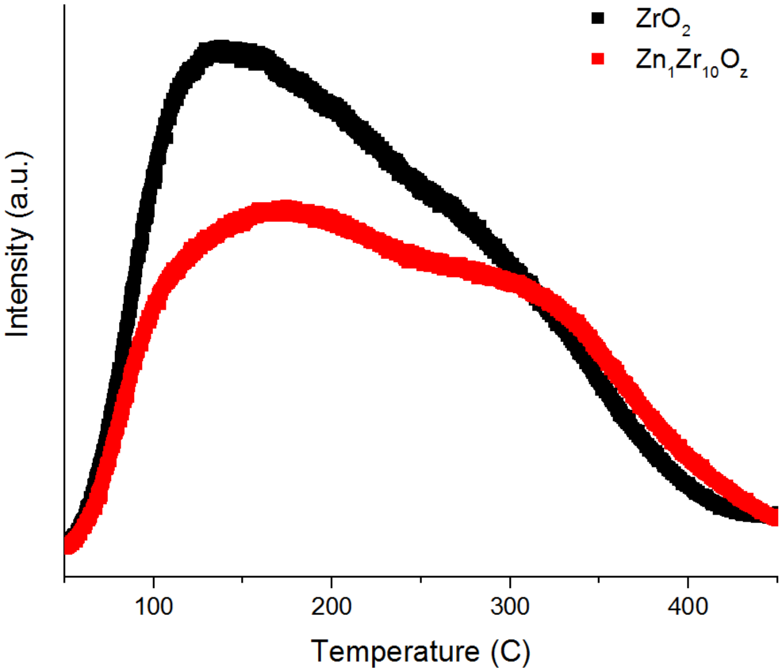


Figure S3. CO_2 temperature programmed desorption curves from 50-500 ºC. .

The NH_3 and CO_2 temperature programmed desorption curves show the effect of ZnO addition to ZrO2. In Figure S1, for acidic sites, the addition of ZnO weakens the acidity (at all strengths) of the mixed oxide compared to the single oxide alone. However, Figure S3 shows that the opposite occurs for basic sites with the addition of ZnO. The mixed oxide shows fewer weak basic sites but the addition of ZnO maintains the number of stronger basic sites and even slightly increases the strength of the strongest sites.

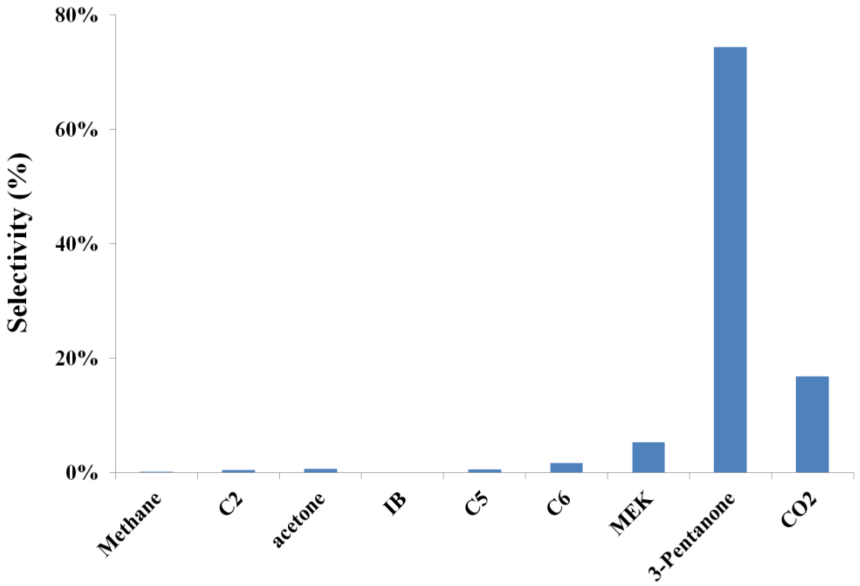


Figure S4. Product distribution of the propanoic acid reaction over $Zn_1Zr_{10}O_z$. Reaction conditions: 100 mg, T=415 °C, S/C=5, $P_{\text{propanoic acid}}$ = 0.62 mol %, WHSV = 0.08 $g_{\text{acid}} * g_{\text{catal}}^{-1} * h^{-1}$.

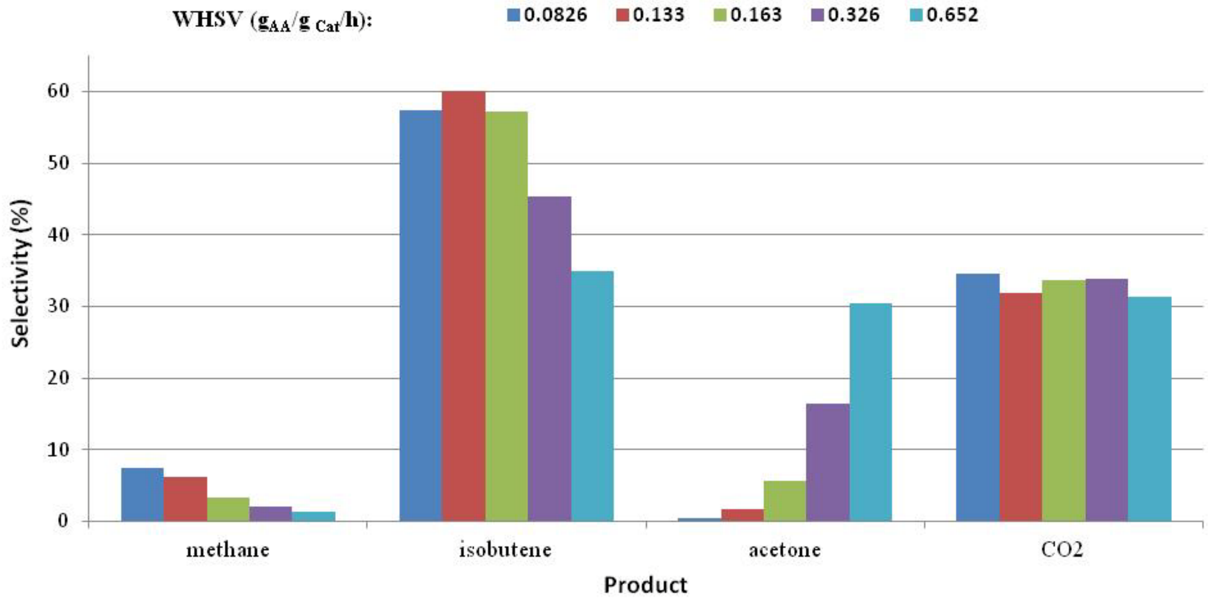


Figure S5. Effect of residence time on acetic acid to isobutene conversion. (*800 mg* $Zn_1Zr_{10}O_z$, T= 415 °C $P_{\text{acetic-acid}}$ ***=8.3%,*** *S/C=2.5. Carbon Balance = 85%-93%*

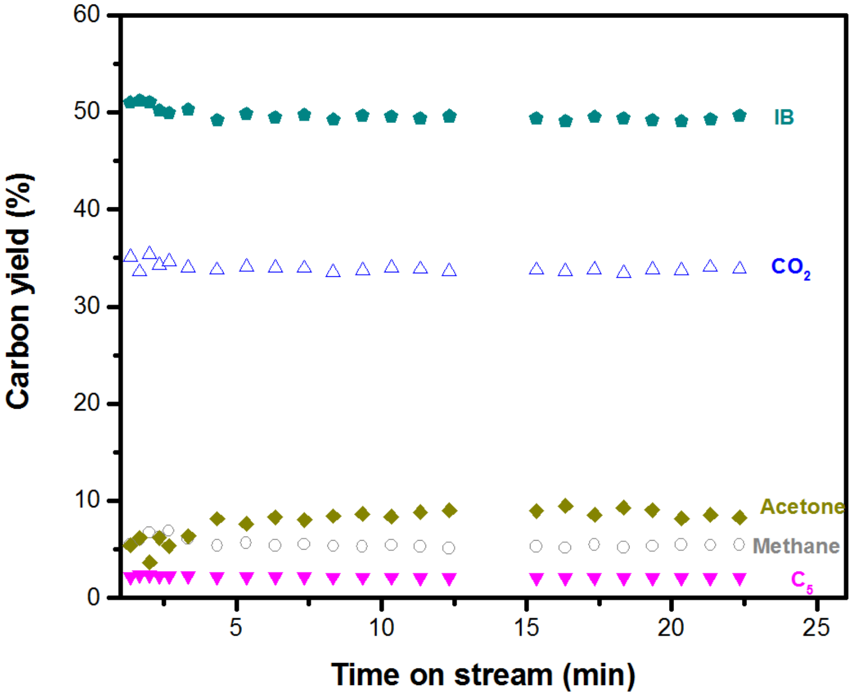


Figure S6. Stability of $Zn_1Zr_{10}O_z$ with an acetic acid feedstock derived from fermentation. Reactions conditions: 100 mg catalyst, $P_{AA\text{-equivalent}}$= 0.70 mol %, WHSV =0.105 $g_{acetic\ acid} \bullet g_{catal}^{-1} \bullet h^{-1}$ T=415 °C. Carbon balance is ~94%.

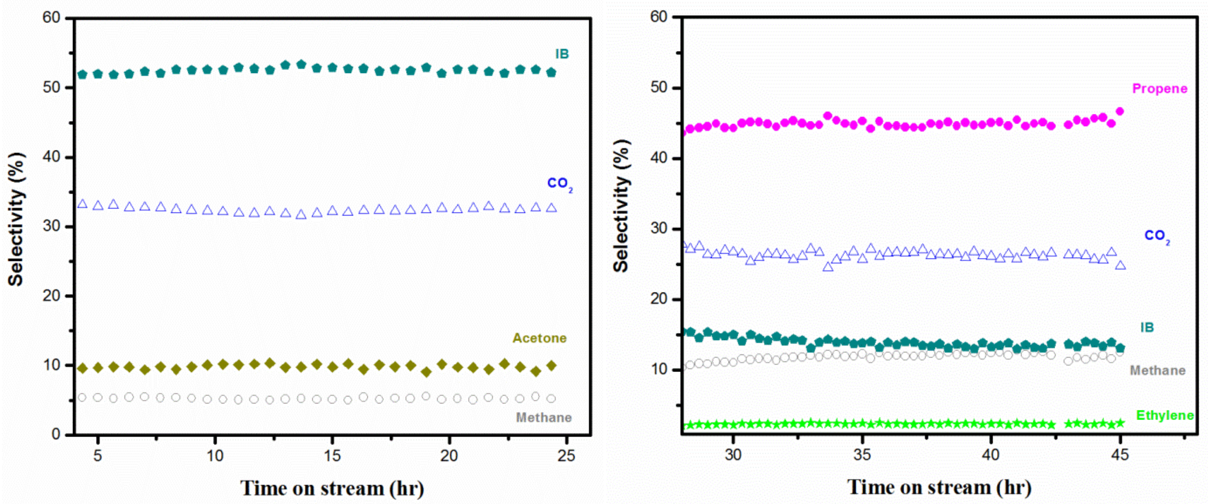
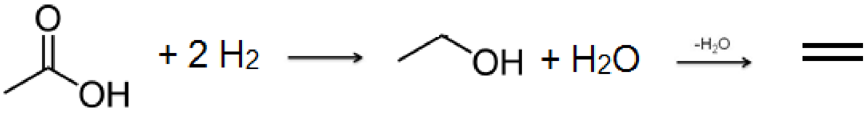


Figure S7. Stability of $Zn_1Zr_{10}O_z$ with an acetic acid feedstock without (left) and with H_2 cofeeding (right). Reactions conditions: 100 mg catalyst, $P_{AA\text{-equivalent}}$= 0.63 mol %, Without H_2 cofeeding: WHSV =0.101 $g_{acetic\ acid} \cdot g_{catal}^{-1} \cdot h^{-1}$ T=415 °C; With H_2 cofeeding: WHSV = 0.253 $g_{acetic\ acid} \cdot g_{catal}^{-1} \cdot h^{-1}$, T=450 °C, Carbon balances for without and with co-feeding H_2 is ~90% and ~70%, respectively.



Scheme S1. Reaction mechanism proposed for ethylene from acetic acid over $Zn_xZr_yO_z$ with H_2 co-feeding.

1. J. Sun, R. A. Baylon, C. Liu, D. Mei, K. J. Martin, P. Venkitasubramanian and Y. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 507-517.