Supplementary Information

Efficacy of mechanochemically prepared ceria-zirconia catalysts in ketonisation of acetic acid

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1. HPLC Calibration Curves

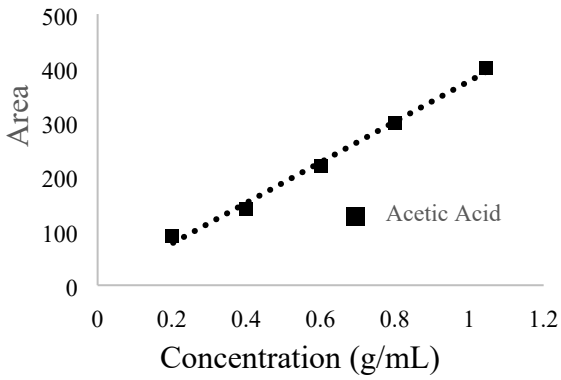


Figure S1. Calibration Curve for Acetic Acid

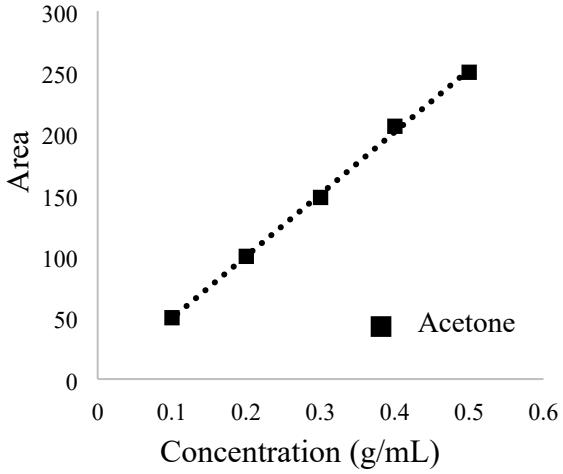


Figure S2. Calibration Curve for Acetone

2. BET

Nitrogen adsorption-desorption isotherms were employed to conduct the BET analysis. The isotherms were measured at a temperature of 77 K using the Microtrac BELSORP-miniX instrument and analysed using the BET equation. The catalyst displayed a Type IV isotherm, indicating the presence of a mesoporous structure as evidenced by the hysteresis loop depicted in **Figure S3**. Additionally, **Figure S4** illustrates the BET isotherm for further examination.

The results of the BET Analysis indicate that the catalyst has a surface area of 66.21m^2/g while the average pore size is 19.07nm.

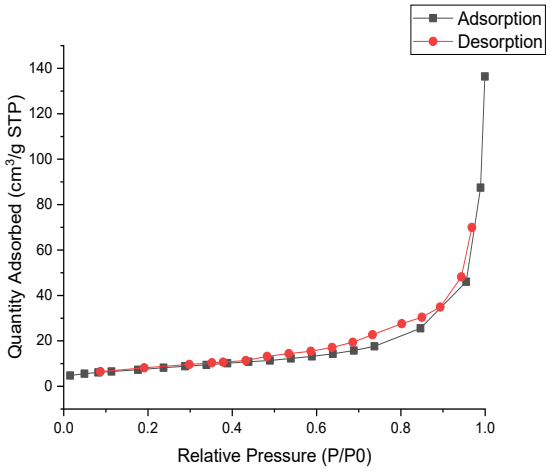


Figure S3. N_2 Adsorption Desorption isotherm

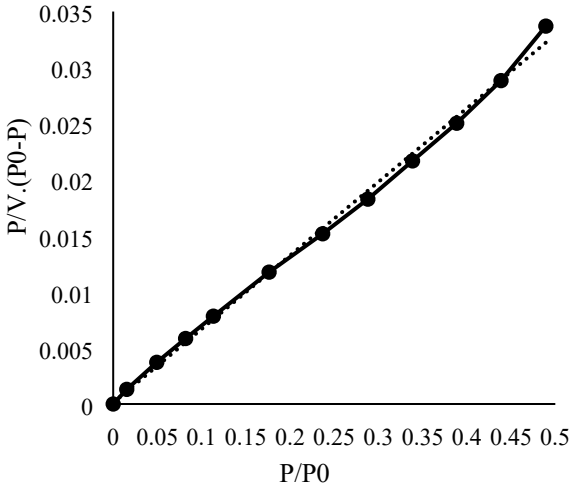


Figure S4. BET Isotherm

3. Particle Size Analysis (DLS)

To determine the catalyst particle size, dynamic light scattering technique was used. The catalyst powder was dispersed in an ethanol solution to estimate the particle size. The results of the DLS analysis were found the particle size to be 340.8 nm. The results can be seen in the **Figure S5**.

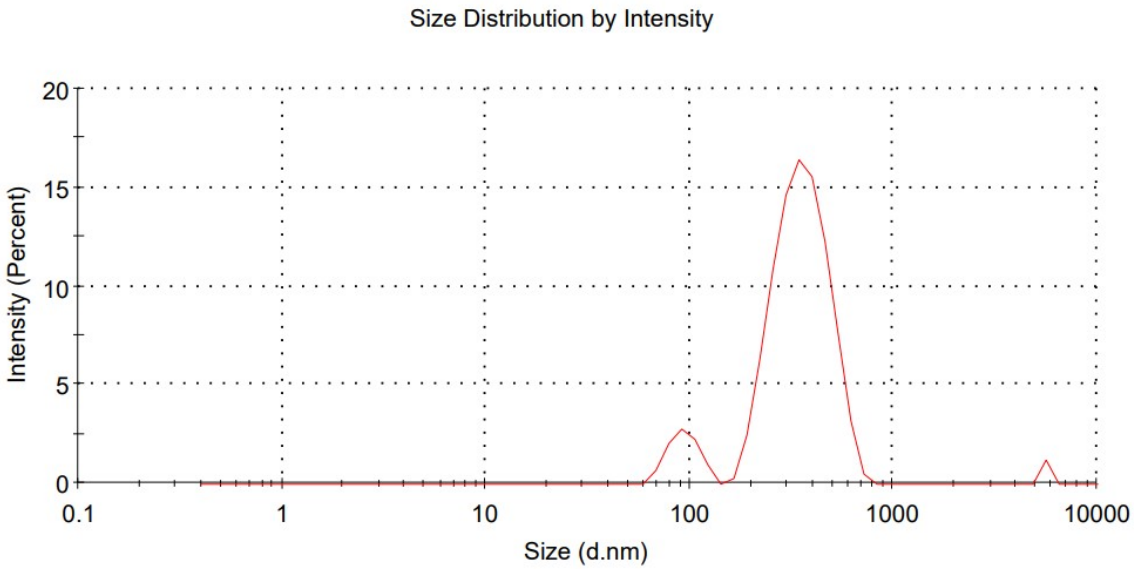
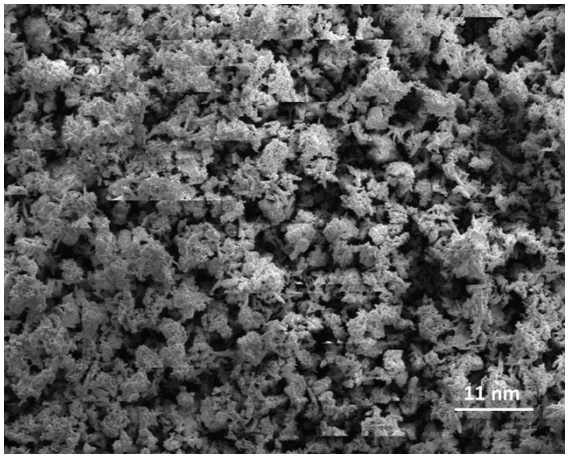


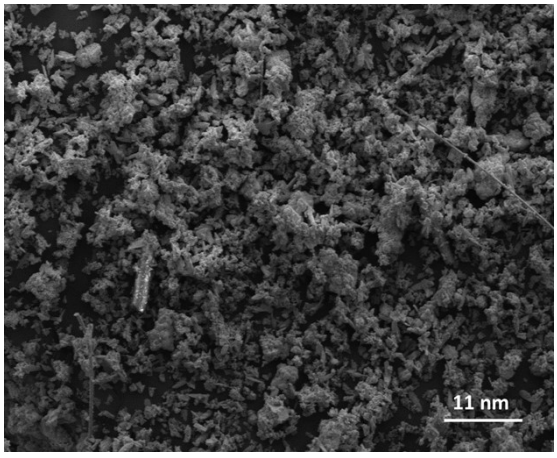
Figure S5. Results of DLS

4. SEM

Scanning electron microscope (SEM) images (**Figure S6**) provide comparative insights into the particle morphologies of the fresh and spent 75CeZr catalysts. Both samples exhibit porous nanoaggregates composed of much smaller primary particles, indicative of high catalytic activity and minimal mass transport limitations. Moreover, the absence of noticeable morphological changes in the spent catalyst highlights the structural robustness and time-on-stream stability of the catalyst under reaction conditions.

B





A

Figure S6. SEM Imaging of (A) Fresh Catalyst (B) Spent Catalyst

5. Parity Plots

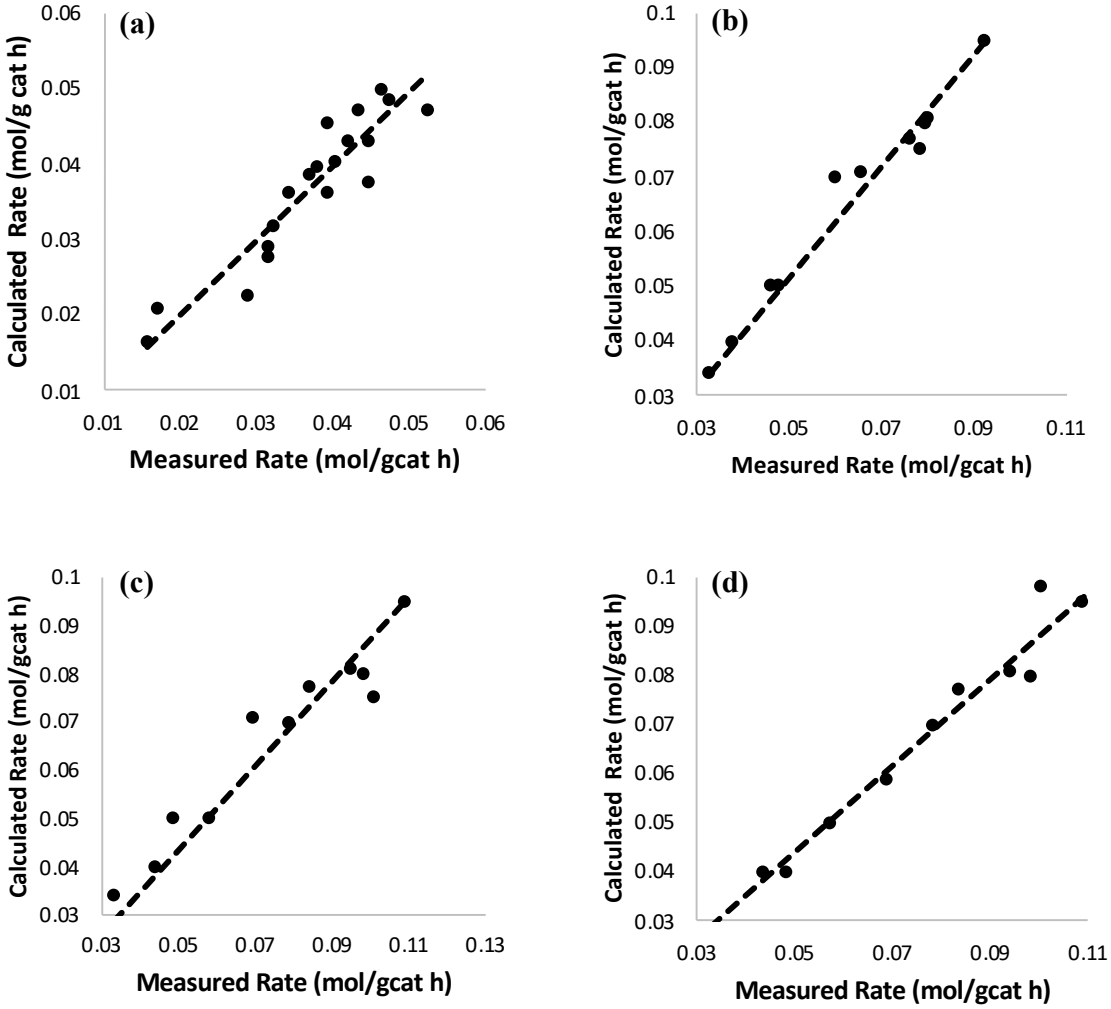


Figure S7. Parity Plots for ketonisation reactions performed at different temperatures, (a) 300 ℃, (b) 325 ℃, (c) 350 ℃, and (d) 375 ℃.

6. Mass Transport Limitations

To ensure the accuracy of kinetic parameters that can be utilized for evaluating a given reaction mechanism, it is crucial to carry out measurements in a mass transfer limitations-free environment. The mass transfer limitations for estimating the chemical kinetics were estimated by the Mears Criteria for external diffusion limitations and Weisz-Prater criteria for internal

diffusion limitations. The Mears Criteria states that if the value of $\chi<0.15$, then external mass transfer can be neglected. The following methodology has also been followed by Pandey et al.

$$\chi = \frac{-r_A^{'} \rho_b Rn}{k_c C_{Ab}}$$

Equation 6.1. Mears Criteria for External Mass Diffusion

r_A= Measured Rate of Reaction=1.31×10^{-5} kmol/kg cat.s (from rate calculations)

ρ_b=Bulk Density of Catalyst =5314 kg/m^3 (from catalyst characterization section)

ρ_{cat}=Catalyst Density = 6500 kg/m^3 (from catalyst characterization section)

Volume of Catalyst = V_C= $3.763\times10^{-7}m^3$ (calculated by known mass and density of catalyst)

Dp= Internal Diameter of reactor= 0.006m

L=Length of catalyst bed=0.045m

Volume of Reactor =V_R= $\pi Dp^2 \times L/4$= 0. $1.272\times10^{-6}m^3$

Φ=Volume of Catalyst / Volume of Reactor =V_C/V_R= 0.2958

R= Average radius of Catalyst particle 1.7×10^7m (from catalyst characterization section)

N=Order of Reaction = 2 (reaction order)

K_c = 2.816 m/s (estimated from Frossling Correlation)

C_{ab}= 17.47 kmol/m^3

The value of Mears criteria is 1.15×10^{-9} much lower than the required value of 0.15 thus eliminating the external mass transfer diffusion limitation.

The Frossling Correlation for estimating the mass transfer coefficient is as follows,

$$Sh = 2 + 0.6R_e^{1/2}Sc^{1/3}$$

Equation 6.2. Frossling Correlation for Mass Transfer Coefficient

$Sh=k_c\, d_p/D_{AB}$, (Sherwood Number)

Here k_c is the mass transfer coefficient (m/s) d_p is the diameter of catalyst particle (m) and D_{AB} is the Diffusivity (m^2/s). It should be emphasized that the diffusivity utilized in this study is the effective diffusivity, which is the Knudsen Diffusivity. This is due to the catalyst powder's small pore diameter of 19.07nm (from BET Measurement), which is significantly less than the mean free path of acetic acid (320nm), rendering Knudsen diffusion as the dominant mass transfer mechanism. The D_{Kn} value is estimated by $D_{Kn}=v\, d_p/3$, 'v' denotes the average

velocity of acetic acid molecules in the gas phase at 673 K and 1 atm (calculated from kinetic theory of gasses to be 27.052m/s) using the formula $V_{avg}=\sqrt{8KT/\pi M}$, while 'dp' represents the average pore size diameter of the catalyst. The value of d_p is 2.2×10^{-7}m (From BET) while that of D_{Kn} is $3.5\times10^{-7}m^2/s$.

$$R_e=u_a\, d_p/\upsilon, \text{ (Reynold's Number)}$$

Here, u_a is the actual velocity of gas in the reactor, which is the product of bed porosity and superficial gas velocity. The superficial gas velocity has been calculated based on the flowrate and cross sectional area of the reactor. The term υ is the kinematic viscosity of acetic acid 6.58×10^{-7} m/s.

$$Sc= \upsilon/D_{AB} \text{ (Schmidt Number)}$$

The values of Re, Sc and Sh are 0.00078, 6.12 and 3.85 respectively for this sample calculation. Here, the terms are kinematic viscosity and Diffusivity as described previously. In a similar fashion, the Weisz-Prater criteria was evaluated by the correlation given below. The internal diffusion can be ignored if the value of $\varphi<0.3$. In this case the value for all cases was found to be 0.008 much lesser than the actual value thus confirming the absence of internal mass transfer limitations.

$$\varphi = \frac{r_{obs}\rho_p R_P^2}{D_e C_{AS}}$$

Equation 6.3. Weisz Prater Criteria for Internal diffusion

In this context, 'r' denotes the rate of reaction per unit volume, while 'R_p' signifies the average radius of the catalyst particle. The variable 'C_{AS}' represents the acetic acid concentration on the catalyst surface, whereas 'D_e' refers to the effective diffusivity, which in this study, is the Knudsen diffusivity as previously discussed. Lastly, 'ρ_p' denotes the density of the catalyst particle. All the values are taken for the same test case as shown in the Mears Criteria.