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

Supplementary File

Untangling the Active Sites in Exposed Crystal Facet of Zirconium Oxide for Selective Hydrogenation of Bioaldehydes

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Table S1. The composition of monoclinic and tetragonal phases and crystallite size of various ZrO_2 catalysts.

Entry No.	Catalyst	Monoclinic phase (%)[a]	Tetragonal Phase (%)[a]	Crystallite size (nm)[b]	Yield of FOH (%)
1	M-ZrO_2-U-C	100.0	0	14.3	85.5
2	T-ZrO_2-U-C	16.8	83.2	18.5	34.2
3	M-ZrO_2-U-N	100	0	14.2	89.8
4	T-ZrO_2-U-N	5.6	94.4	23.6	8.1

[a] Phase composition was calculated using the equation given below

$$v_m = \frac{1 \cdot 311}{1 + 0.311} x, \quad v_t = 1 - v_{m,} \quad x = \frac{I_m[-111] + I_m[111]}{I_m[-111] + I_m[111] + I_t[111]}$$

[b] The crystallite size of various ZrO_2 catalysts was calculated using Debye Scherrer equation given below

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

Table S2. The ratio of exposed facet of selected ZrO_2 catalysts.

Catalyst	Ratio of (-111)/ (111) facet[a]
M-ZrO_2-U-N	1.51
M-ZrO_2-U-C	1.44
T-ZrO_2-U-N	0.07

[a] Obtained from the XRD peaks appeared at 2θ of 28.2 and 31.5° for (-111) and (111) facet, respectively.

Table S3. CO_2-TPD data of various ZrO_2 catalysts.

Catalyst	Basic sites (µmol/g)			Total basic sites (µmol/g)	Yield FOH (%)
	Weak (50-200) °C	Medium (200-350) °C	Strong (350-750) °C		
M-ZrO_2-U-C	110	127	161	398	85.5
T-ZrO_2-U-C	103	91	120	314	34.2
M-ZrO_2-U-N	139	144	238	521	89.8
T-ZrO_2-U-N	51	33	154	238	8.1
ZrO_2-C	9	4	3	16	0.72

Table S4. Kinetic data derived from the first-order rate equation.

Temp. (K)	FFA Conversion at different time (min)					Rate constant
	30	60	120	240	360	1000*k (s^{-1})
348	14.7	16.8	32.3	38.3	53.6	1.8
383	33.4	46.1	61.7	75.7	92.4	6.2
398	46.0	59.0	74.6	88.5	99.99	23.5

Table S5. Activation energy calculated using the Arrhenius equation and comparison with the previous work.

Temp. (K)	Activation energy, Ea ($kJmol^{-1}$)	Catalyst	Ref.
348			
383	49.0	M-ZrO_2-U-N	Present Work
398			
413	70.5	ZrPN	[1]
413	79.1	ZrO_2	[1]
358	60.7	Zr-Beta	[2]

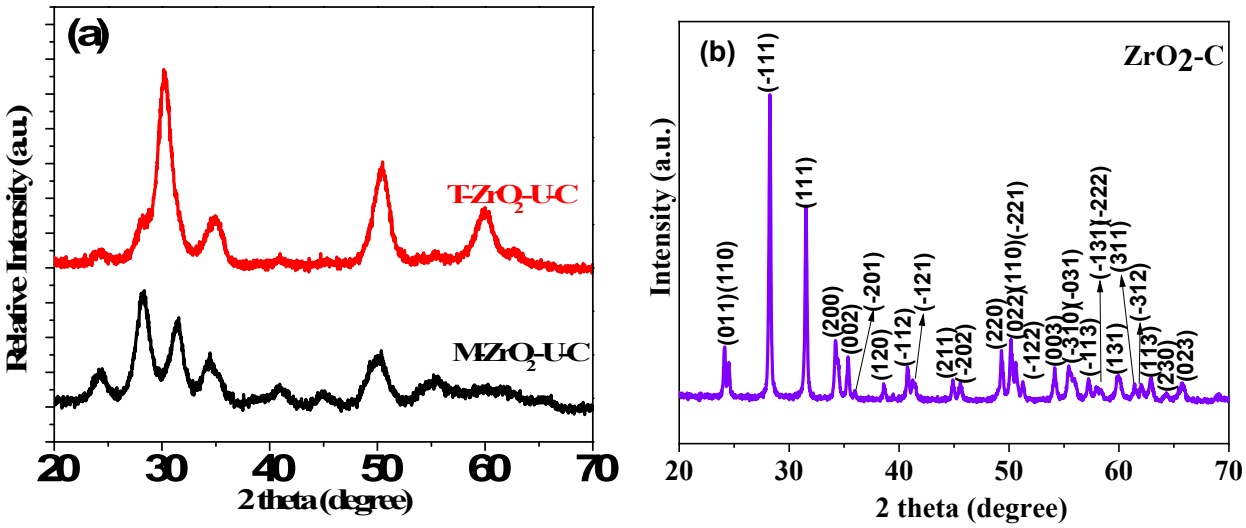

Figure S1. (a) Combined XRD patterns of M-ZrO_2-U-C, T-ZrO_2-U-C, and (b) XRD pattern of ZrO_2-C.

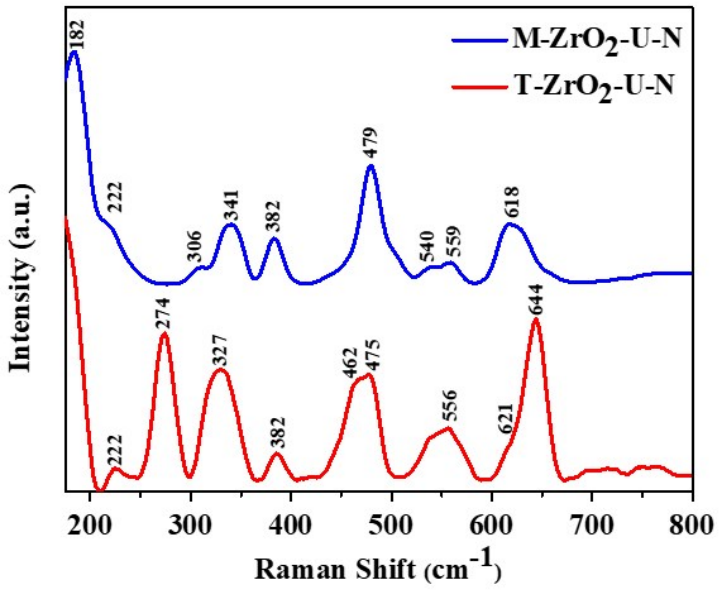

Figure S2. Raman spectra of M-ZrO_2-U-N and T-ZrO_2-U-N.

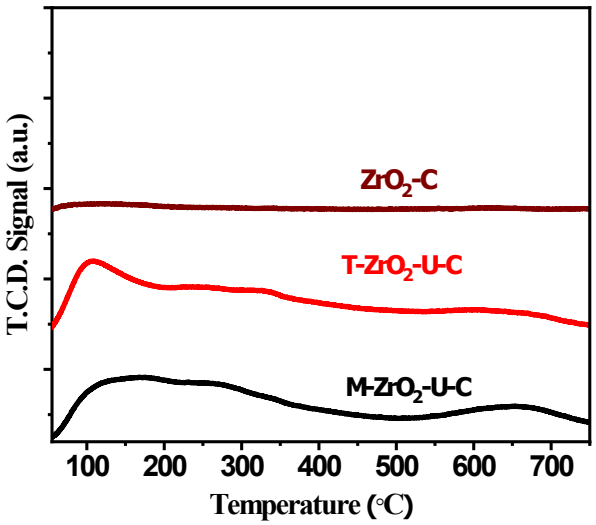

Figure S3. CO_2-TPD profile of various ZrO_2 catalysts.

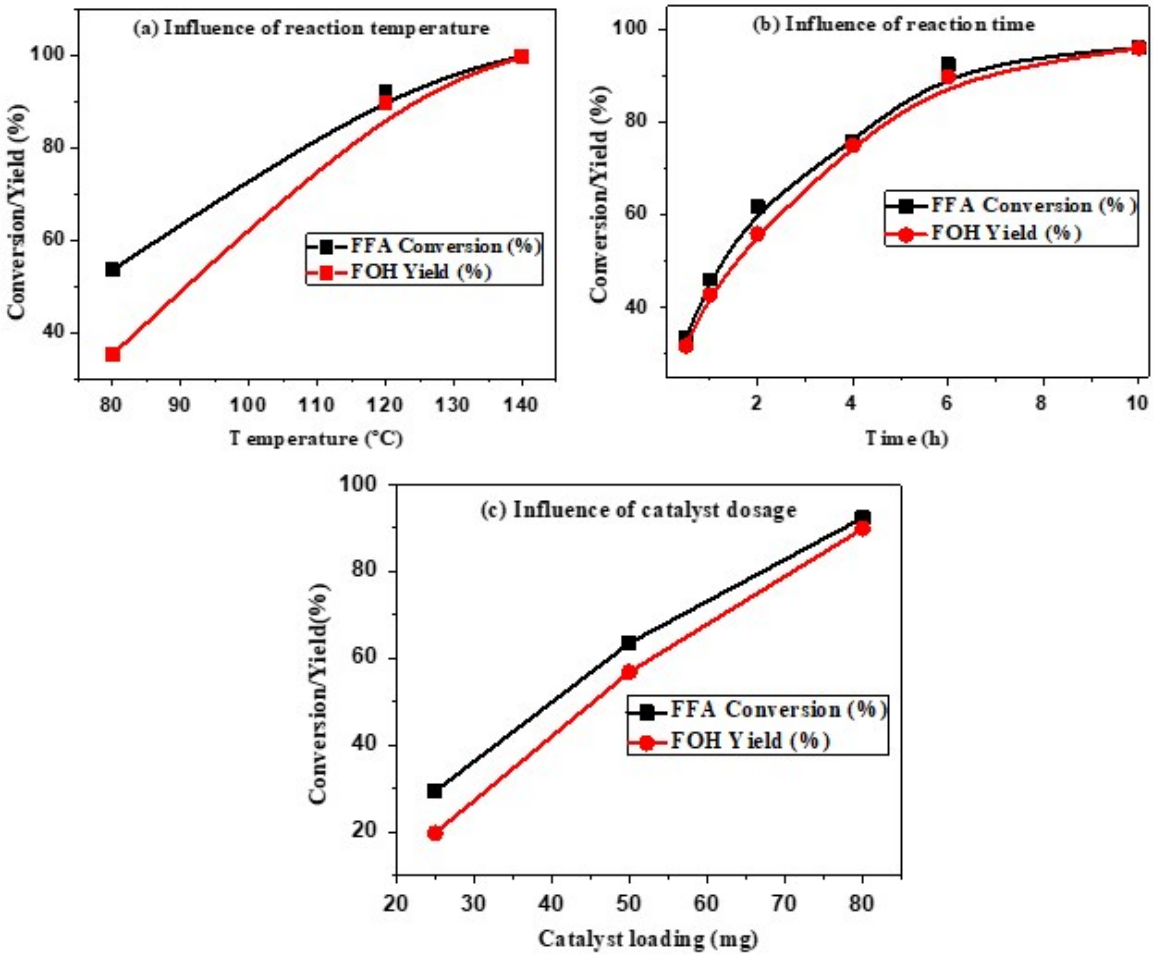

Figure S4: (a) The influence of reaction temperature (Reaction conditions: 1 mmol furfural, 80 mg M-ZrO_2-U-N, 4 ml isopropanol, 6 h), (b) time (Reaction conditions: 1 mmol furfural, 80 mg M-ZrO_2-U-N, 4 ml isopropanol, 110 ºC and (c) catalyst dosage (Reaction conditions: 1 mmol Furfural, 4 ml isopropanol, 110 °C, 6 h).

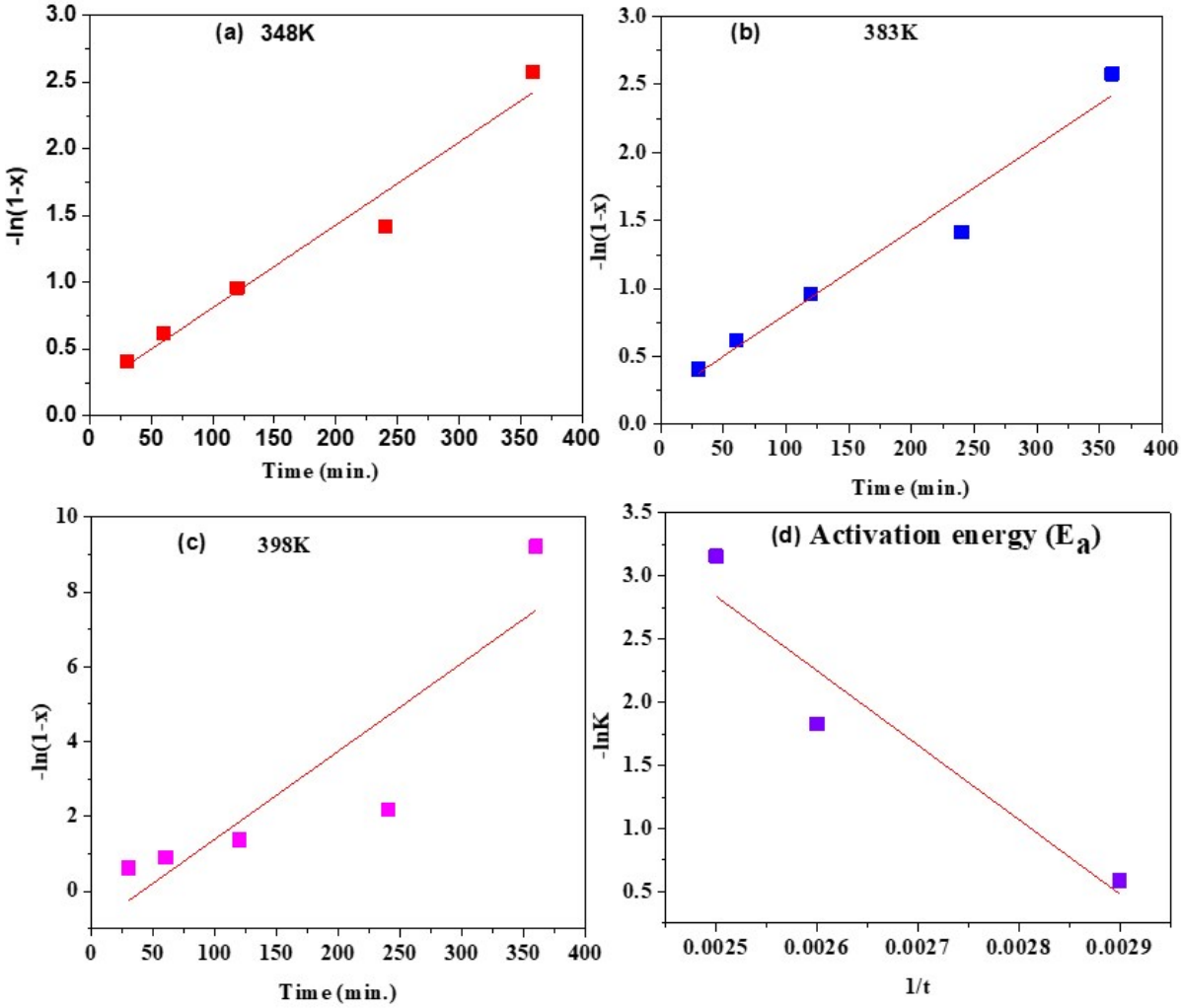

Figure S5. Plotting –ln(1-x) as a function of time at various temperatures (a) 348 K, (b) 383 K and (c) 398 K, and (d) Plotting –lnK against 1/T to calculate activation energy using Arrhenius equation.

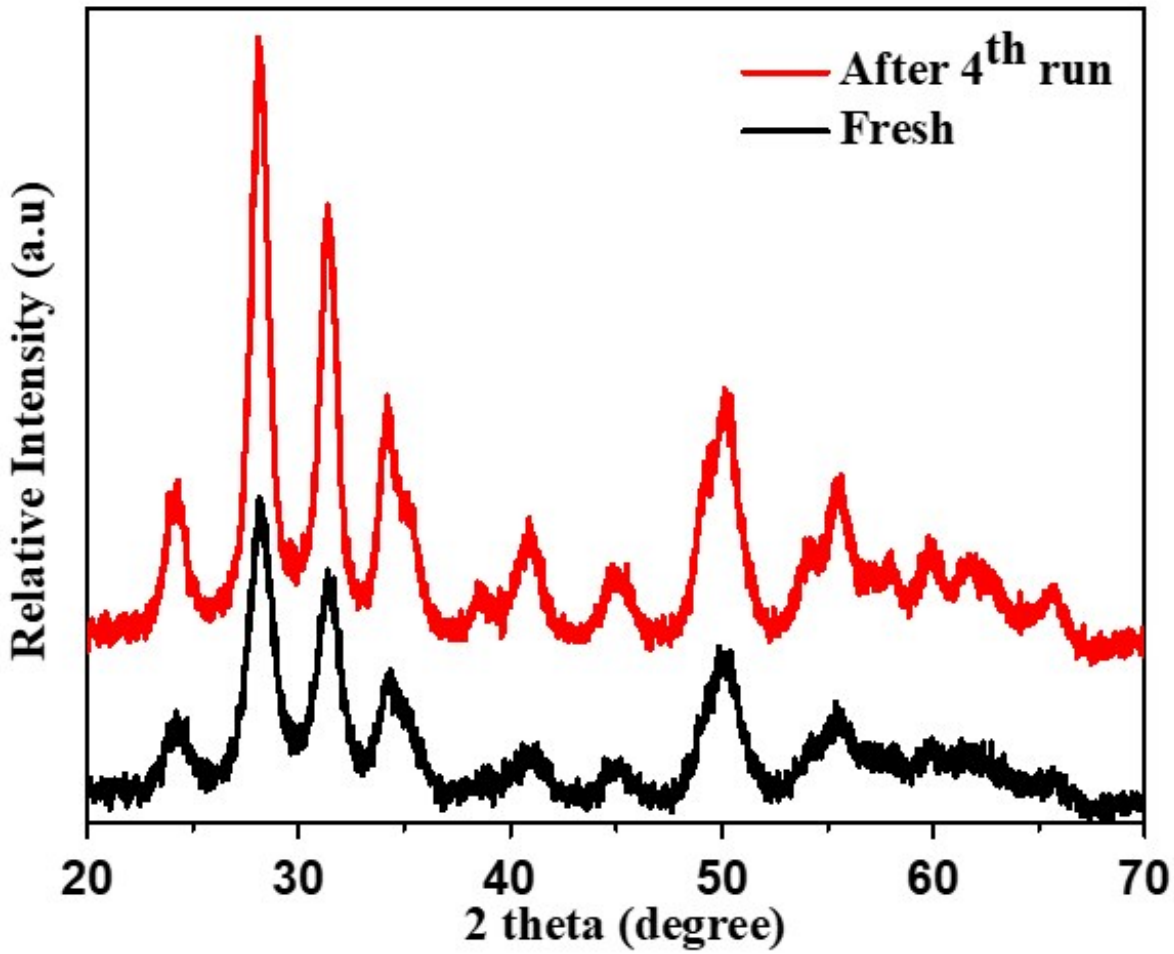

Figure S6. X-ray diffraction pattern of the fresh and recovered catalyst after the fourth run.

References

(1) Li, H.; He, J.; Riisager, A.; Saravanamurugan, S.; Song, B.; Yang, S.; *ACS Catal.* **2016**, 6, 7722-7727.

(2) Koehle, M.; Lobo, R. F.; *Catal. Sci. Technol.* **2016**, 6, 3018-3026.