Green Chemistry

Electronic Supporting Information for

Efficient Conversion of Bio-renewable Citric Acid to High-value Carboxylic Acids on Stable Solid Catalysts

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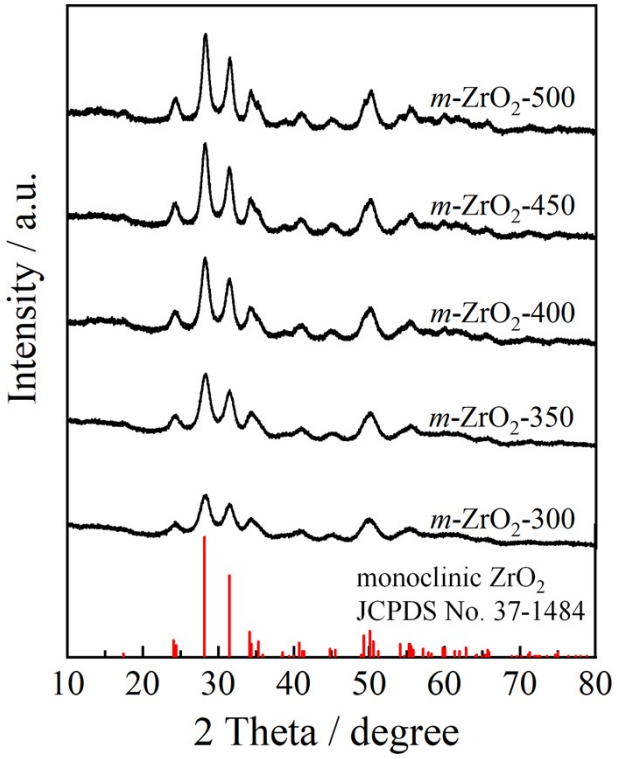

Fig. S1 XRD patterns of *m*-ZrO_2 samples calcined at different temperatures in the range of 300-500 ^oC.

The spectra confirm that the monoclinic structure of the ZrO_2 was obtained, according to the JCPDS No. 37-1484.

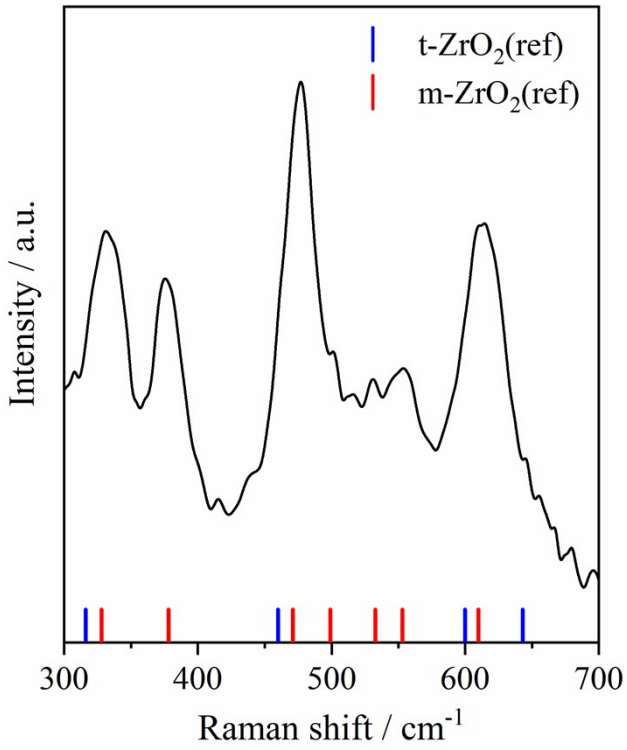

Fig. S2 Raman spectrum for *m*-ZrO_2-300.

The representative peaks at 328, 378, 471, 499, 533, 553, and 610 cm^{-1} are Raman scattering of *m*-ZrO_2, further confirming the formation of monoclinic phase.[1] Unfortunately, the Raman spectrum of *t*-ZrO_2 was not obtained due to the strong fluorescence background.

Reference

1. L. Bai, F. Wyrwalski, C. Machut, P. Roussel, E. Monflier and A. Ponchel, *CrystEngComm*, 2013, **15**, 2076-2083.

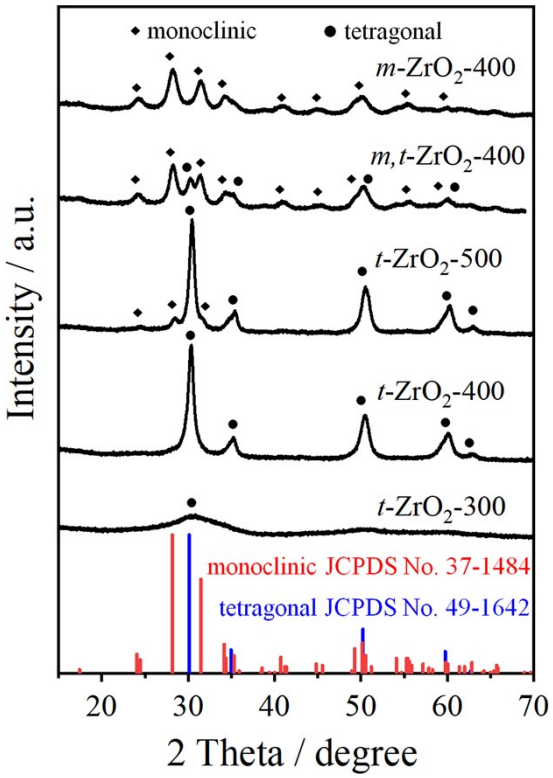

Fig. S3 XRD patterns of *m*-ZrO_2-400, *m,t*-ZrO_2-400, *t*-ZrO_2-300, *t*-ZrO_2-400, and *t*-ZrO_2-500.

The diffraction peaks of *m*-ZrO_2-400 were almost identical to those of *m*-ZrO_2-300 (Fig. S1). Compared with *m*-ZrO_2-400, a new diffraction peak at 30.3° in the pattern of *m,t*-ZrO_2-400 was observed, which can be assigned to the representative (011) lattice plane of *t*-ZrO_2, demonstrating the successful synthesis of *m,t*-ZrO_2 containing mixed monoclinic and tetrahedral phases

For *t*-ZrO_2-300, only one diffraction peak at 30.3° can be observed. With increasing the calcination temperature to 400 °C and 500 °C, the intensity was greatly enhanced, together with other typical diffraction peaks of *t*-ZrO_2 at 35.2°, 50.5°, 60.2° and 62.9°, indicating the successful synthesis of *t*-ZrO_2. It seems that a pure tetragonal phase can only be formed at a calcination temperature at 400 °C in the calcination temperature range of 300 to 500°C. Therefore, in Table 2, the ZrO_2 samples obtained at 400 °C were used as the catalysts to discuss the impacts of different crystallites on the reaction performance.

Table S1 BET specific surface area and acid-basic densities of different ZrO_2 catalysts.

ZrO_2	BET surface area (m^2/g)	Acidic site (μmol/g)	Basic site (μmol/g)	Acidic density (μmol/m^2)	Basic density (μmol/m^2)
m-ZrO_2-300	213.6	295.3	245.3	1.38	1.14
m-ZrO_2-350	154.6	291.0	146.3	1.88	0.95
m-ZrO_2-400	135.1	216.7	117.1	1.60	0.86
m-ZrO_2-450	98.7	185.9	80.1	1.88	0.81
m-ZrO_2-500	83.4	117.6	61.1	1.41	0.73
t-ZrO_2-400	94.3	120.3	124.0	1.27	1.31
m,t-ZrO_2-400	91.4	123.2	61.0	1.35	0.67

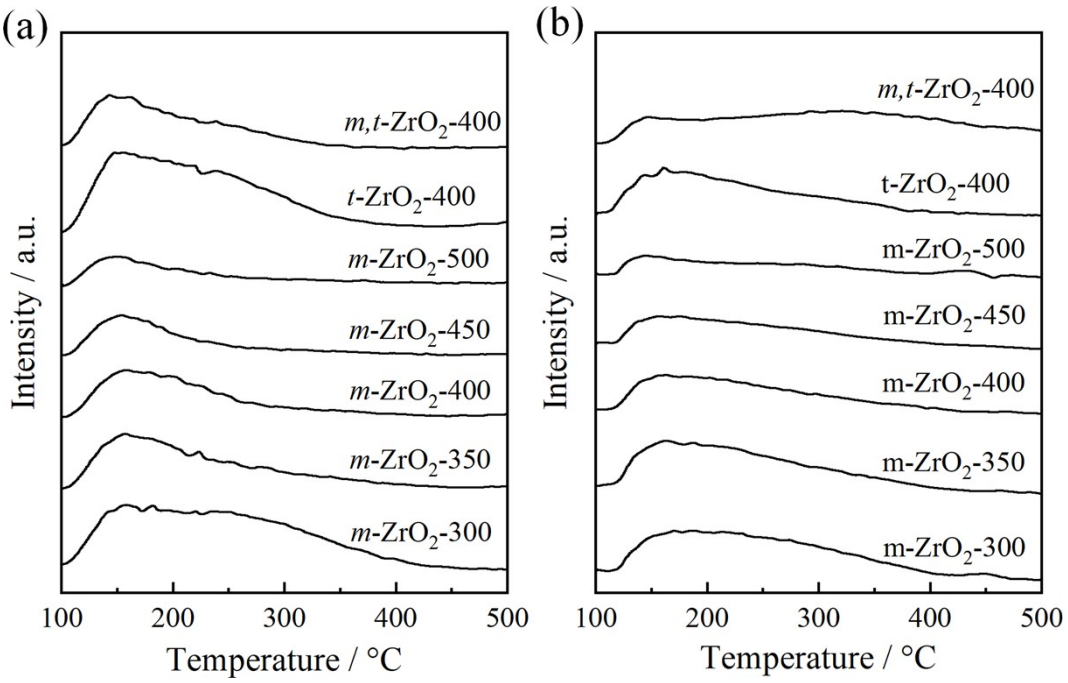

Fig. S4 (a) CO_2- and (b) NH_3-TPD of *m*-ZrO_2-T catalysts.

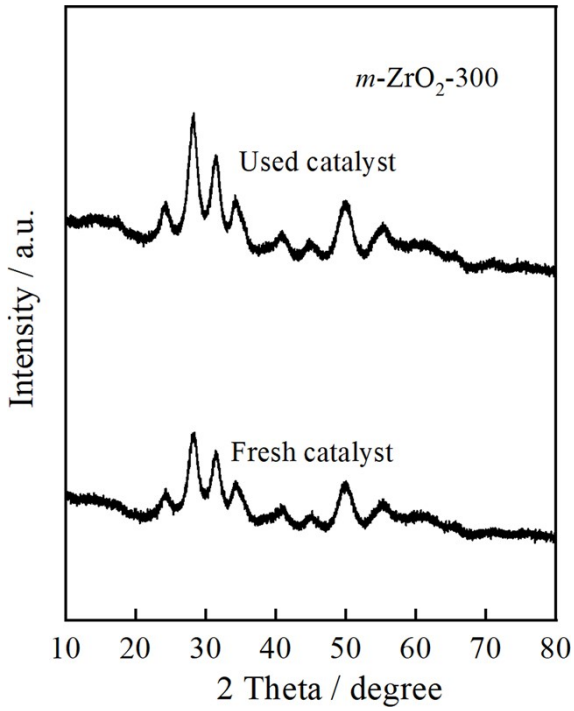

Fig. S5 XRD patterns of *m*-ZrO_2-300 before and after five consecutive cycles in the conversion of citric acid to ICA. Reaction conditions: 1 mmol citric acid, 0.3 g *m*-ZrO_2-300, 20 mL water, 2 MPa N_2, 180 °C, 40 min. ICA: itaconic acid.

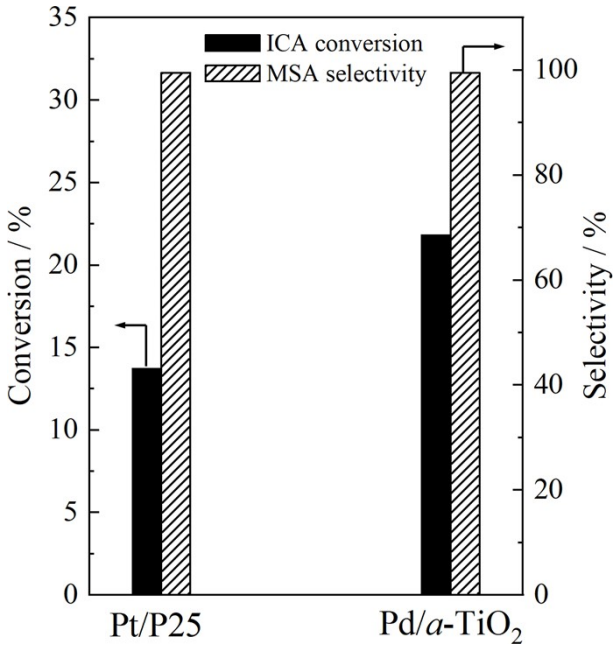

Fig. S6 Comparison of activity of Pt/P25 and Pd/*a*-TiO_2 in the hydrogenation of ICA. Reaction condition: 5 mmol ICA, 0.05 g catalyst, 20 mL water, 2 MPa H_2, 25 °C, 10 min. ICA: itaconic acid; MSA: 2-methylsuccinic acid.