

Electronic Supporting Information

for

Effect of the C_α substitution on the ketonic decarboxylation of carboxylic acids over *m*-ZrO₂: the role of entropy

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Kinetic study of the influence of acid partial pressure on reaction rate. The ketonic decarboxylation of pentanoic acid and 2-methyl-butanoic acid was studied in separate reactions over *m*-ZrO₂ in a fixed-bed continuous-flow reactor using different partial pressures, i.e. acid:N₂ ratios in the feed flow. The initial reaction rate can be described by:

$$r_0 = \frac{k K_A [acid]}{1 + K_A [acid]}$$

Where *k* is the kinetic constant and *K_A* is the adsorption constant of the acid on the catalyst surface. If acid adsorption is strong, that is, *K_A* [acid] ≫ 1, then *r₀* ~ *k*, and the rate of ketone formation will be independent of the partial pressure of acid in the feed flow. The reaction rate as a function of acid partial pressure *P_{acid}* is plotted in Figure S1 for both acids. In both cases, a 15-fold increase in *P_{acid}* results in a reaction rate only ~1.3 times larger, which means that under the reaction conditions chosen the catalyst surface is saturated with substrate molecules and the initial reaction rate *r₀* can be approximated to the kinetic constant *k*, that is, *r₀* = *k*.

$$k = \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}}$$

$$\Delta G = \Delta H - T \Delta S$$

$$k = \frac{k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{\frac{-\Delta H^\ddagger}{RT}}$$

$$\ln k = \ln\left(\frac{k_B T}{h}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{R} \left(\frac{1}{T}\right)$$

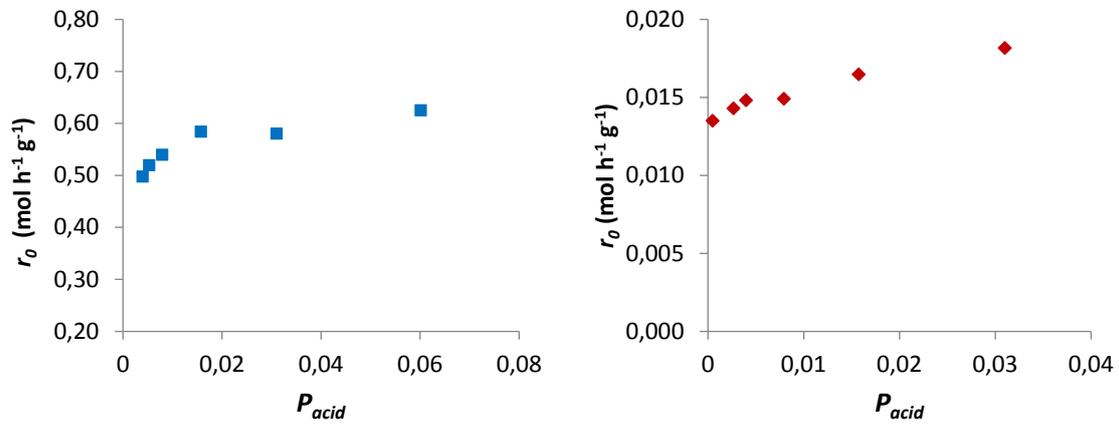


Figure S1. Plot of initial reaction rates r_0 (in mol h⁻¹ g⁻¹) for ketonic decarboxylation of pentanoic (blue ■) and 2-methylbutanoic (red ◆) acids as a function of partial pressure of the acid P_{acid} in the feed flow. Reaction conditions for pentanoic acid: $W = 0,1$ g catalyst, mass flow rate = 44,640 g h⁻¹ acid; for 2-methylbutanoic acid: $W = 2,5$ g catalyst, mass flow rate = 22,512 g h⁻¹ acid. $T = 698$ K.

DFT study of pivalic acid dehydroxylation. Dehydroxylation of pivalic acid, taken as the most sterically hindered C₅, adsorbed over *m*-ZrO₂ occurs through a transition state similar to that previously described for acetic acid, in which dissociation of the C–OH bond and formation of a new C–Os bond occur simultaneously (see Figure S2), with no steric hindrance due to the three substituting methyl groups. The optimized values of the C–OH bond lengths in the transition states for dehydroxylation of acetic and pivalic acids are 1.45 and 1.46 Å, respectively, and the corresponding DFT-D3 calculated intrinsic activation energies are 37 and 33 kJ mol⁻¹.

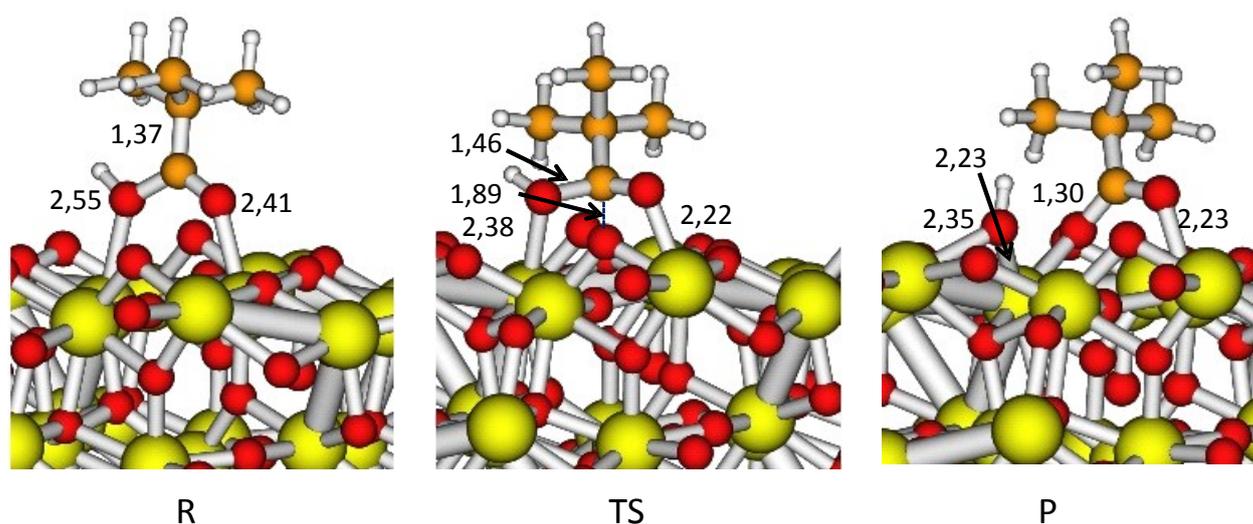


Figure S2. PW91 optimized geometries of reactant, transition state and product of pivalic acid dehydroxylation over *m*-ZrO₂. Selected distances in Å. Zirconium, oxygen, carbon and hydrogen atoms are depicted as yellow, red, orange and white balls, respectively.

Computational details. The surface of monoclinic zirconia (*m*-ZrO₂) was modeled using a periodic ($\bar{1}11$) facet slab model previously described in detail.¹ The unit cell contains three ZrO₂ layers and has a chemical composition of Zr₄₈O₉₆. Geometry optimizations were performed at the periodic PW91 level fixing the coordinates of the Zr and O atoms in the two lowermost ZrO₂ layers, whereas all other atoms were fully relaxed until forces were below 0.015 eV Å⁻¹. Only one irreducible **k**-point and a plane wave basis set with an energy cut off of 500 eV were used in the calculations. The optimization of the transition-state structure was performed with the dimer method using only first derivatives.² Electronic PW91 energies were further corrected by addition of the intermolecular dispersion energies, which were evaluated using the D3 method³ over the PW91 optimized geometries.

References

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- (2) G. Henkelman, H. Jónsson, *J. Chem. Phys.* 1999, **111**, 7010.
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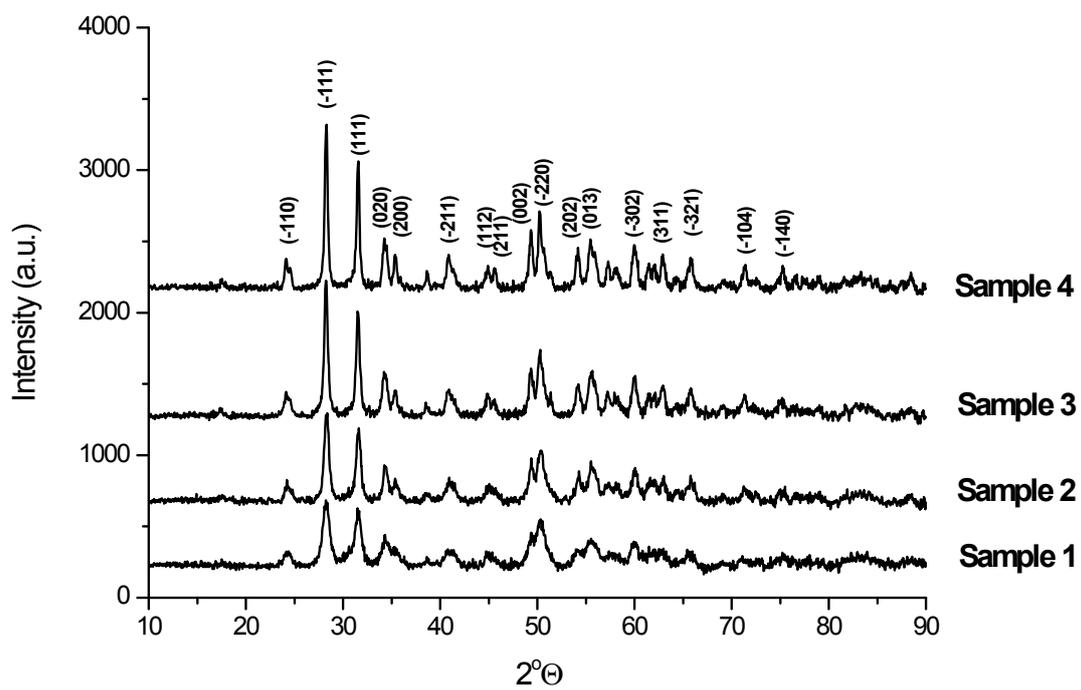


Figure S3. XRD diffractograms of the four m-ZrO₂ samples obtained by calcination at increasing temperatures.