

Electronic Supplementary Information

**Catalytic deoxygenation of fatty acid *via* ketonization and α -carbon scissions
over layered alkali titanate catalysts under N_2**

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Proton exchange/exfoliation/reassembling

The treatment of $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ with HCl produces the protonic $H_{1.6}Ti_{1.6}O_4 \cdot 0.8H_2O$ as reported and characterized previously.¹⁻³ This treatment involves the exchange of K^+ ions with $H^+ \cdot H_2O$ and the leaching of intralayer Zn.²⁻⁴ XRF analyses indicated that the product after proton exchange contains (all values in wt%) 0.21% K_2O , 1.04% ZnO , and 98.6% TiO_2 . This contrasts with 19.0% K_2O , 16.3% ZnO and 63.0% TiO_2 in as made “ $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ ”, which translates to the experimental composition $K_{0.74}Zn_{0.34}Ti_{1.45}O_4$. Accordingly, a 100-fold reduction in the potassium content and a ~94% removal of Zn cation can be deduced. So, the complete proton exchange can be assumed, and the small amount of remaining Zn is neglected. The composition is $Ti_{0.993}Zn_{0.010}K_{0.004}O_2$, or simply $Ti_{0.99}Zn_{0.01}O_2$.

An amount of 0.4 g of $H_{1.6}Ti_{1.6}O_4 \cdot 0.8H_2O$ was mechanically shaken with 100 mL of diluted TBAOH (mol TBA^+ /mol H^+ = 1) at room temperature for 2 weeks.^{2, 3} The mixture gradually turned into a milky suspension. This white colloid exhibits the Tyndall effect (Fig. S1i) and shows the characteristic light absorption at $\lambda_{max} = 266$ nm (Fig. S1ii). This indicates the exfoliation of microcrystals into individual $Ti_{0.8}O_2^{0.8-}$ nanosheets^{2, 3, 5} (*i.e.*, simply TiO_2 nanosheets). To a 100 mL of this colloid, 100 mL of 2 M KOH was added dropwise, resulting in white precipitates which were left in the mother liquor overnight. Then, the precipitates were filtered, washed until free from excess hydroxide ions, and dried at room temperature overnight. This was then calcined in air at 450 °C for 6 h, giving the reassembled TiO_2 catalyst.

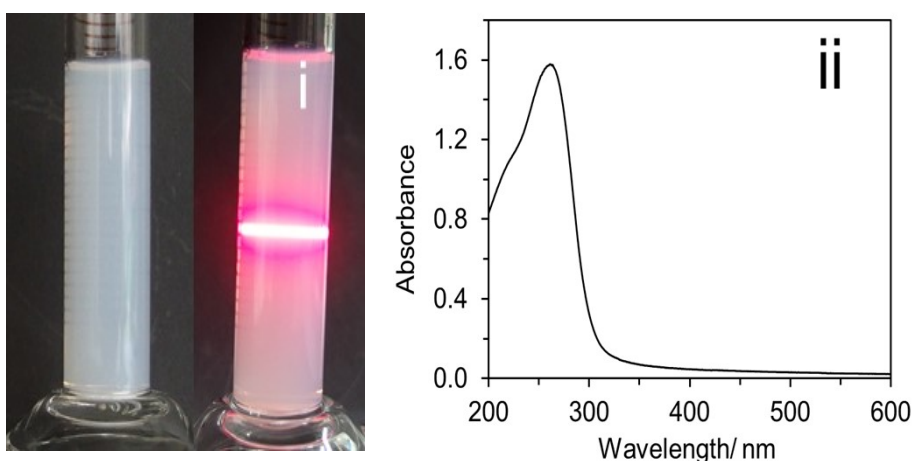


Fig. S1 (i) Photographs of the lepidocrocite-type TiO_2 nanosheets colloid without (left) or with (right) the laser light shined on demonstrating the Tyndall effect, (ii) the UV-vis absorption spectrum of the colloid.

Raman spectra

The Raman spectrum of reassembled TiO_2 in Fig. S2iii is the overlap of signals due to lepidocrocite titanate (at 287 cm^{-1}) and anatase^{6, 7} (143 , 190 , 401 , 513 and 639 cm^{-1}). The former is actually coincides with that in the as made $\text{K}_{0.8}\text{Zn}_{0.4}\text{Ti}_{1.6}\text{O}_4$ shown in Fig. S2i, where the whole pattern is typical of alkali lepidocrocite titanate.^{8, 9} In both cases, the local structure was preserved after their use as a catalyst (compared Fig. S2i,ii and Fig. S2iii,iv), in good agreement with the XRD results in Fig. 1 in the manuscript.

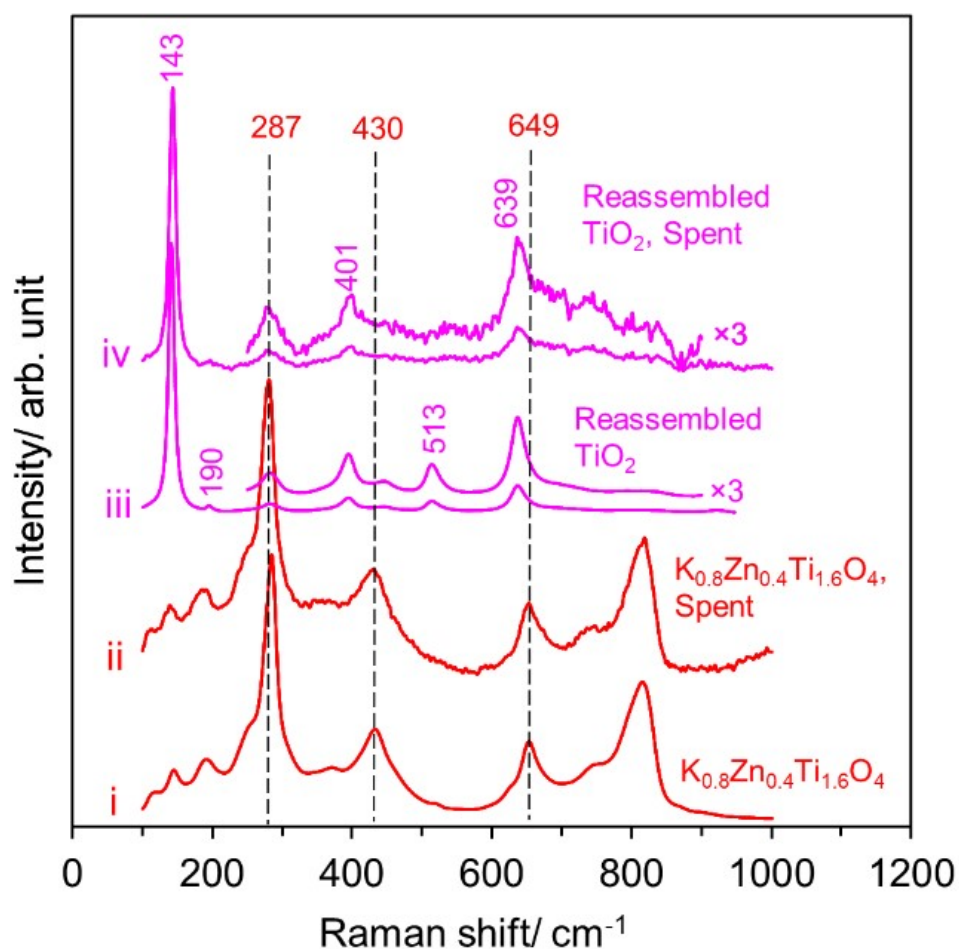


Fig. S2 The Raman spectra of: (i) $\text{K}_{0.8}\text{Zn}_{0.4}\text{Ti}_{1.6}\text{O}_4$, (ii) spent $\text{K}_{0.8}\text{Zn}_{0.4}\text{Ti}_{1.6}\text{O}_4$, (iii) reassembled TiO_2 , and (iv) spent, reassembled TiO_2 . Raman spectra were recorded using a DXR Smart Raman (ThermoScientific) at the laser wavelength of 532 nm and the laser power of 5 mW.

Thermogravimetric analyses

The spent $\text{K}_{0.8}\text{Zn}_{0.4}\text{Ti}_{1.6}\text{O}_4$ shows a mass loss of $\sim 10\text{wt}\%$ which we ascribed to coke, similar to the spent reassembled TiO_2 as shown in Fig. S3.

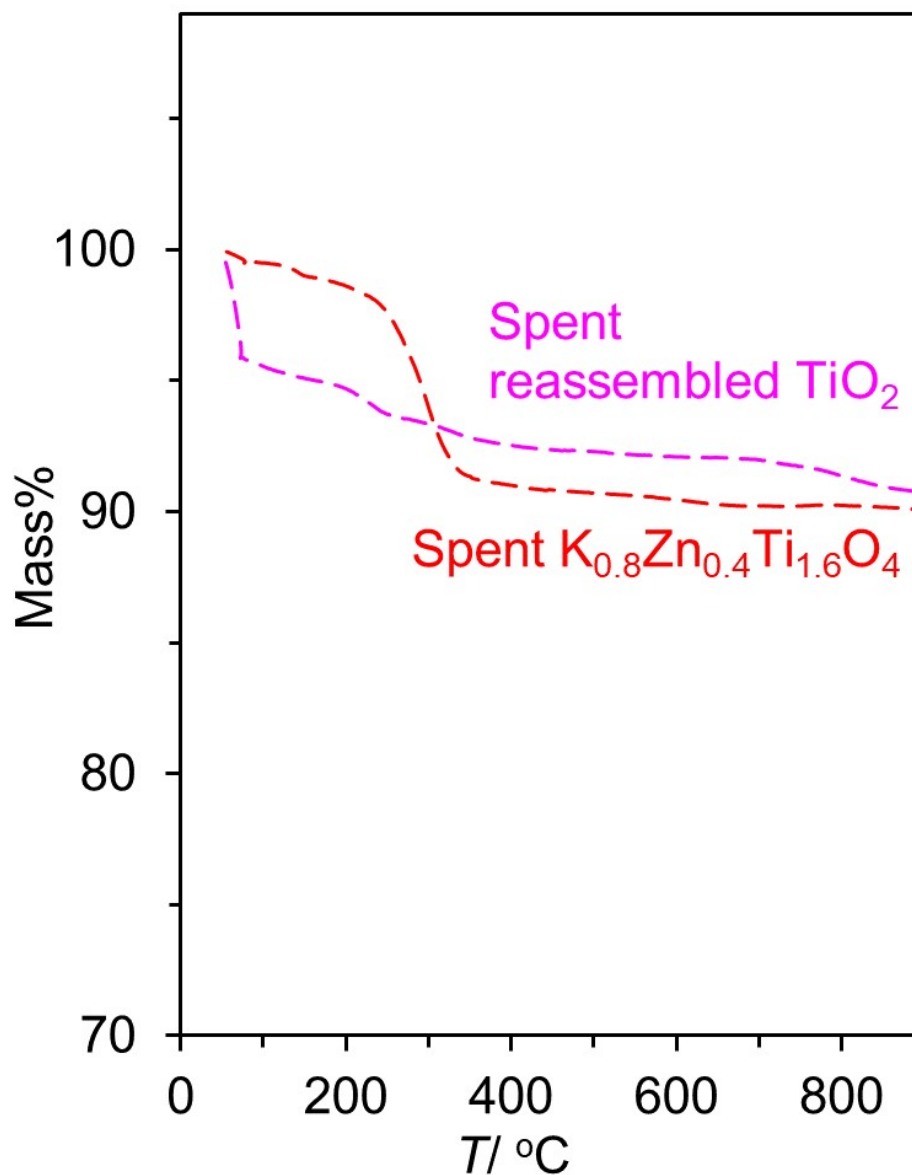


Fig. S3 The mass loss curves of spent $\text{K}_{0.8}\text{Zn}_{0.4}\text{Ti}_{1.6}\text{O}_4$ and spent, reassembled TiO_2 . Thermogravimetric analysis was performed under the flow of N_2 gas (20 mL/min) from RT to 900 °C (10 °C/min) using a Perkin-Elmer, Pyris-1 instrument.

NH₃ temperature-programmed desorption

K_{0.8}Zn_{0.4}Ti_{1.6}O₄ (specific surface area 3 m²/g) shows virtually zero desorption of NH₃. Only a background was observed in the desorption profile. This is in contrast to anatase-type TiO₂ (specific surface area 6 m²/g) with a clear NH₃ desorption (taken from our previous work⁸). Note that the different sample masses was employed, as also indicated in Fig. S4.

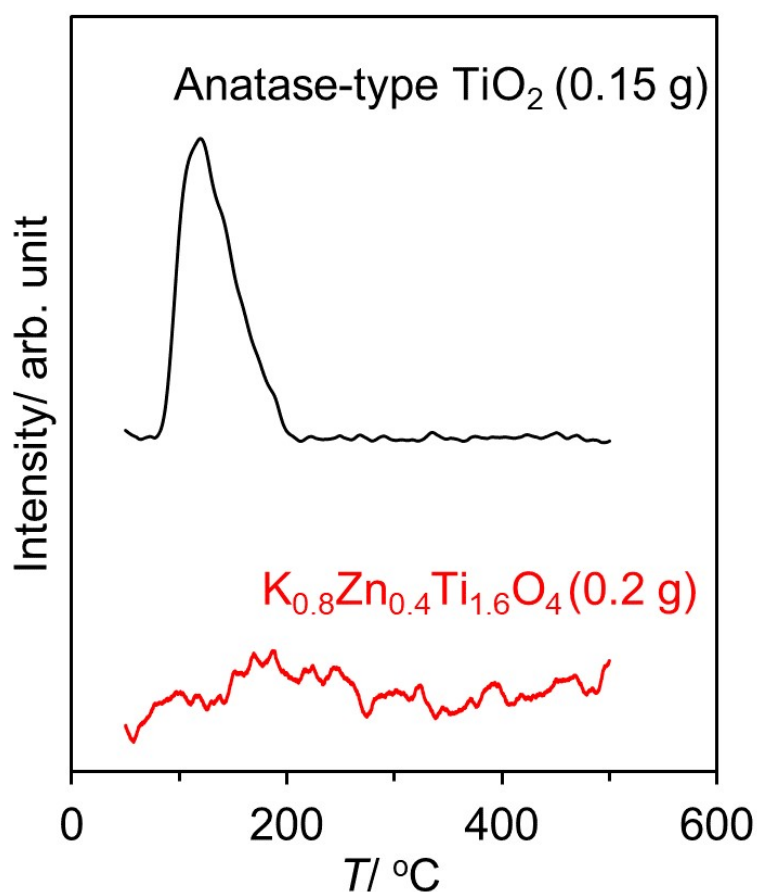


Fig. S4 The NH₃ desorption profiles from K_{0.8}Zn_{0.4}Ti_{1.6}O₄ and anatase-type TiO₂⁸. The sample was loaded into the center of a quartz tube reactor and covered with quartz wool. The sample was activated at 400 °C for 2 h and cooled to ~30 °C (both under air flowing at a rate of 10 °C/min), followed by the adsorption of 1%NH₃/He (50 mL/min) for 1 h. Then, physisorbed NH₃ was purged with helium (30 mL/min) until the baseline as detected by the thermal conductivity detector was flat, usually for 1 h. The profile was next collected from 50 to 500 °C (10 °C/min) under a flow of helium.

Partial charge-catalytic activity correlation

Fig. S5 is the expanded form of Fig. 5 in the manuscript. Here, the data of reassembled TiO_2 are also shown, situated at the far left. The result suggests that the application of the Sanderson's electronegativity equalization principle is valid only to a closely related composition (implying the closely related structure).

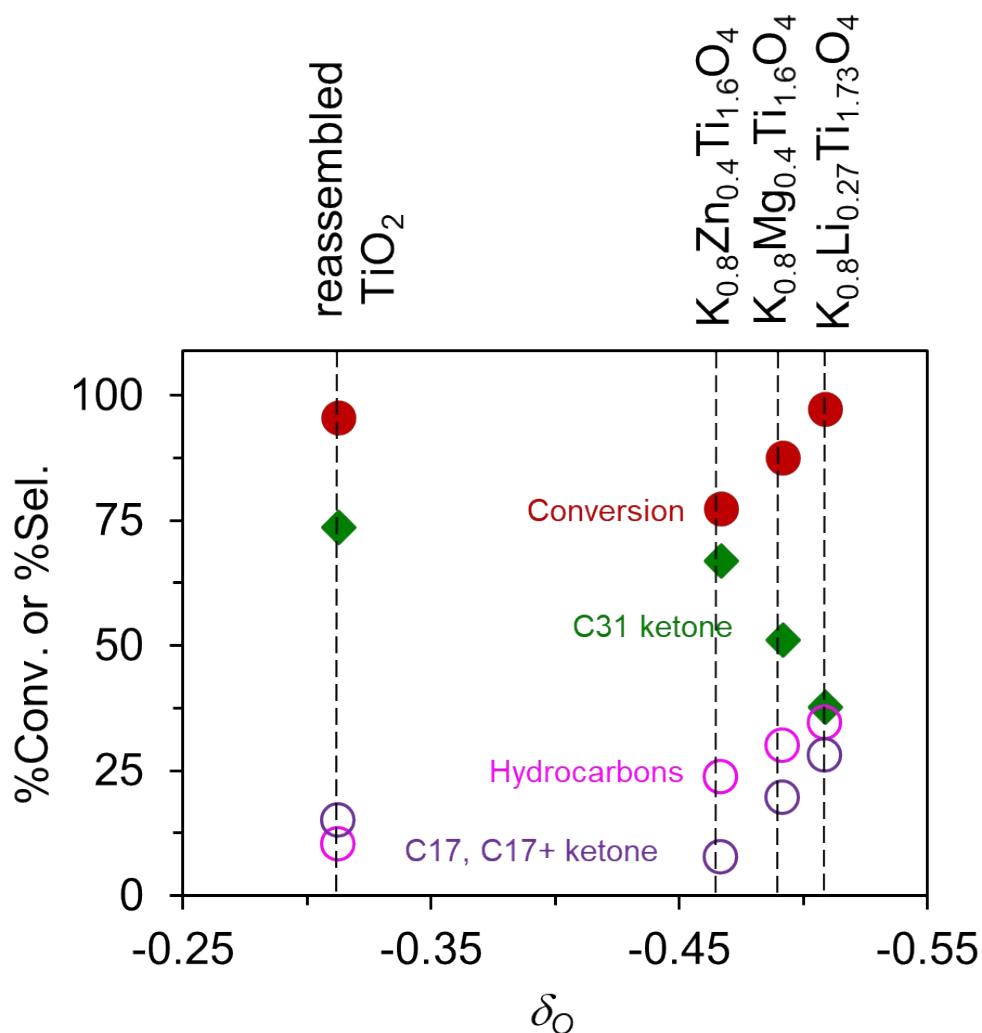


Fig. S5 An expanded view of the δ_{O} -catalytic activity correlation of the three compositions of lepidocrocite titanate and the reassembled TiO_2 .

Comparison of alkane production from ketone scissions

Table S1 Yield of liquid ketone and liquid alkane from the ketone scission of carboxylic acid

Entry	Catalyst/carboxylic acid substrate/ carrier gas ^a	T/ °C	Yield, liquid ketone	Yield, liquid alkane	Ref.
1	Al ₂ O ₃ / C ₈ / N ₂	500	0.3	23.9	10
2	Al ₂ O ₃ / C ₈ / N ₂	450	3.2	34.2	10
3	Al ₂ O ₃ / C ₈ / N ₂	400	0.4	45.8	10
4	Al ₂ O ₃ / C ₈ / N ₂	350	22.2	28.0	10
5	K _{0.8} Li _{0.27} Ti _{1.73} O ₄ / C ₁₆ / N ₂	400	53.2	46.8	This work
6	K _{0.8} Li _{0.27} Ti _{1.73} O ₄ / C ₁₆ / N ₂	375	63.4	33.4	This work
7	K _{0.8} Mg _{0.4} Ti _{1.6} O ₄ / C ₁₆ / N ₂	375	63.7	26.1	This work
8	K _{0.8} Zn _{0.4} Ti _{1.6} O ₄ / C ₁₆ / N ₂	375	57.7	18.3	This work
9	Reassembled TiO ₂ / C ₁₆ / N ₂	375	84.5	9.7	This work
10	Mg,Al mixed oxide/ C ₁₆ / N ₂	375	69.8	22.6	This work

Supplemental references

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