Supporting Information

Elucidation of the roles of water on the reactivity of surface intermediates in carboxylic acid ketonization on TiO_2

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S1. Predominant catalytic contribution from anatase phase in P25 TiO_2

XRD (Figure S1) confirms the predominance of the anatase phase in P25 TiO_2 used in this work. Figure S2 compares the specific rates of acetic acid ketonization (unit per nm^2 per s) on the P25 TiO_2 (Sigma Aldrich, 99.5%), a commercial anatase TiO_2 (US Research Nanomaterials, 99.5%, 5nm), and a commercial rutile TiO_2 (Sigma Aldrich, 99.5%) under similar reaction condition (543 K, 3.5 kPa acetic acid). The reaction rates are similar on P25 TiO_2 and the pure anatase samples, whereas the rutile TiO_2 sample has a much lower rate, about 1/4 of the rate on anatase.

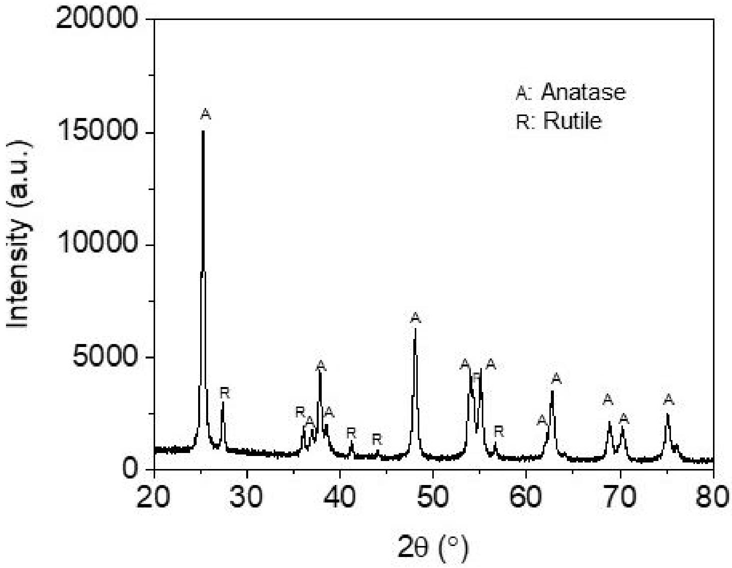

Figure S1. XRD profile of TiO_2(25) catalyst used in this work

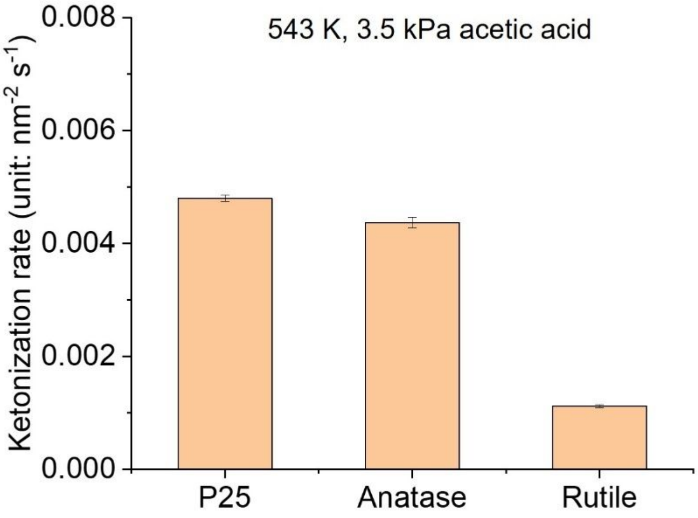

Figure S2. Specific rates of acetic acid ketonization (per nm^2) on TiO_2(P25) (Sigma Aldrich, 99.5%), anatase (US Research Nanomaterials, 99.5%, 5nm), and rutile (Sigma Aldrich, 99.5%) (543 K, 3.5 kPa acetic acid).

S2. DRIFTS

The stability of the surface hydroxyl groups on TiO_2 catalyst was examined with Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Figure S3 shows the DRIFTS spectra of the TiO_2 catalyst before, during, and after 723 K treatment in He. The pristine TiO_2 before treatment shows surface hydroxyl bands at 3696, 3666, and 3631 cm^{-1}. The broad band ranging from 3600 to 3000 cm-1 is ascribed to O-H stretching of H-bonded H_2O molecules on the surface. After heated to 723K, the adsorbed H_2O molecules are removed, but some hydroxyl groups at 3708 and 3660 cm^{-1} still remain on TiO_2 surface, indicating the stability of these surface hydroxyl groups. The shift of the OH peak positions in comparison to the pristine sample is likely associated with the removal of H_2O and higher temperature. After H_2O removal at high temperature, the sample was cooled down to 393K. The two OH peaks shift to higher frequencies at 3720 and 3671 cm^{-1}, respectively.

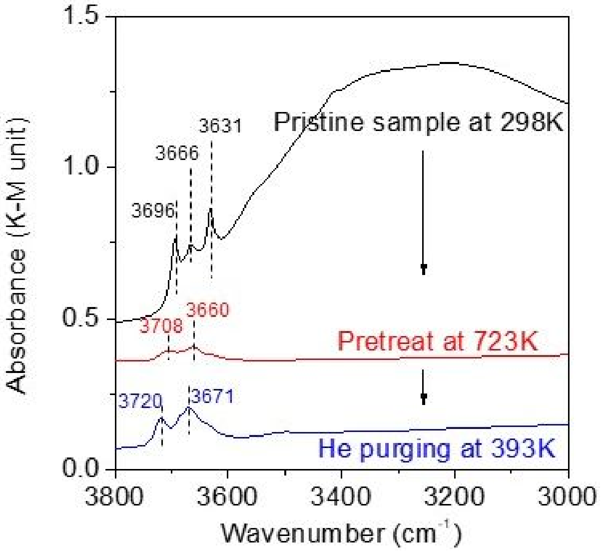

Figure S3. DRIFTS spectra of TiO_2 catalyst pretreated at 723 K followed by cooling to 393 K in He

S3. Acetic acid-TPD

The impact of H_2O on the reactivity of adsorbed acetic acid species on TiO_2 were investigated with adsorption and temperature-programed desorption of acetic acid (acetic acid-TPD). As discussed in the main manuscript, acetic acid-TPD releases the ketonization product acetone. The desorption peak temperature of the dry TiO_2 in He (558K, Figure S4a) is lower than that of hydrated TiO_2 in 1.5 kPa H_2O/He (588K, Figure S4c), the adsorbed acetic acid species are more reactive on dry TiO_2 than on hydrated TiO_2. However, when we pre-hydrated TiO_2 catalysts with 1.5 kPa H_2O at 393 K, followed by conducting acetic acid -TPD in He without cofeeding H_2O vapor (Figure S4b), the TPD profile looked similar to that of dry TiO_2 (Figure S4a). This suggests that it is the molecular H_2O instead of the surface hydroxyl groups that causes activity decrease.

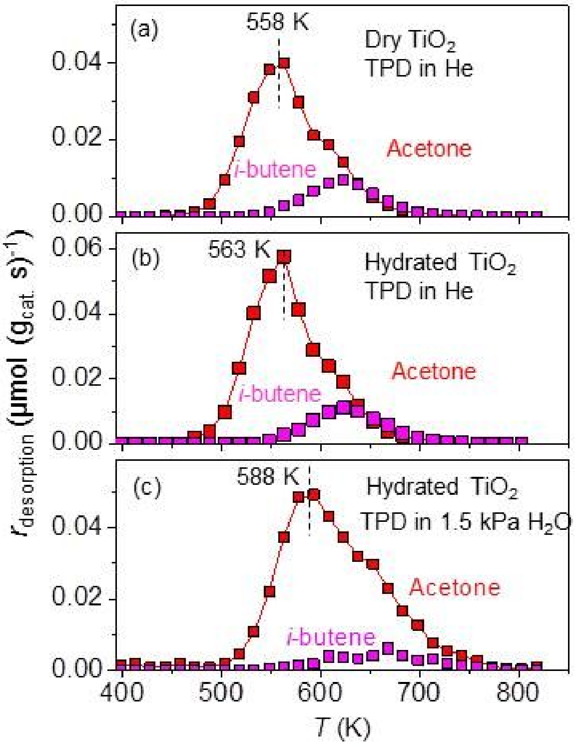

Figure S4. Profiles of acetic acid-TPD on the dry and hydrated TiO_2 catalysts (acetic acid adsorption temperature 393 K): (a) dry TiO_2 with acetic acid adsorption and TPD in He; (b) pre-hydrated TiO_2 with acetic acid adsorption and TPD in He; (c) pre-hydrated TiO_2 with acetic acid adsorption and TPD in 1.5 kPa H_2O/He.

S4. Isobutene formation by acetone reaction on TiO_2

Figure S5 shows the rate of isobutene formation during acetone reaction on TiO_2 catalyst at 623 K as a function of time-on-stream. When acetone was feed as the only reactant feed, deposition of heavy condensation products led to fast catalyst deactivation, so the isobutene formation rate decreases with time-on-stream. Cofeeding 2 kPa of H_2O strongly inhibited the acetone reactions and suppress isobutene formation. The strong inhibition effect was due to the competitive adsorption. Upon stopping H_2O cofeeding, the isobutene formation rate was recovered. This result is in line with the suppression of isobutene formation by introducing water in the acetic acid-TPD, as shown in Figure 7.

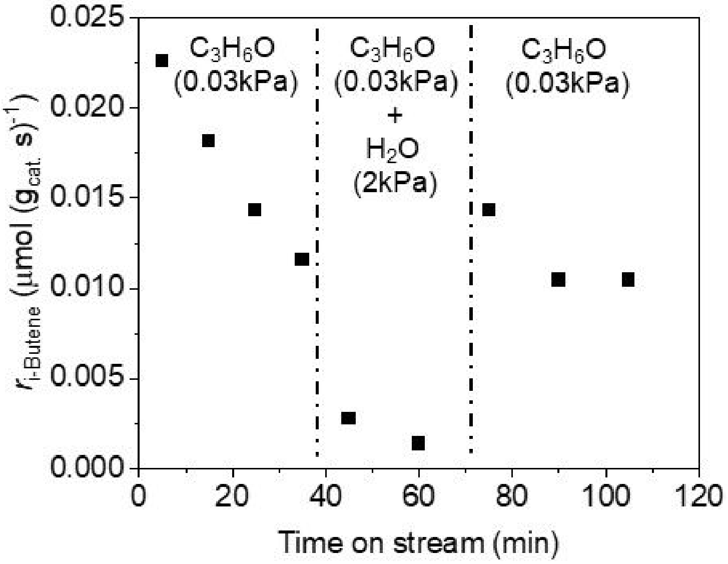

Figure S5. Rate of isobutene formation ($r_{\text{i-Butene}}$) during acetone reaction on TiO_2 as a function of time, with and without cofed H_2O (623 K, acetone pressure 0.03 kPa, cofed H_2O pressure 2 kPa).

S5. NMR

An excess amount of acetic acid addition was used to confirm the assignment as well as the impact on adsorption configurations, shown in Figure S6. It is clearly shown that after adding 6 monolayers of acetic acid on TiO_2 surface, the peak signal at 177 ppm increased, confirming the assignment of molecular acetic acid adsorption. The reason for the slight enhancement in signal is that cross polarization is not able to detect bulk phase acetic acid which maintains random and fast movement. In the meantime, with excessive amount of acetic acid, the chelating bidentate species become more electron-deshielded due to the interaction with molecular acetic acid, manifested by downfield chemical shifting from 188 ppm to 191 ppm. The monodentate acetate species also transformed to bridging bidentate acetate owing to the interaction with excessive molecular acetic acid. These transformation and electron interaction can be the indication that the surface adsorption species is also dependent on the acetic acid partial pressure in the flowing system.

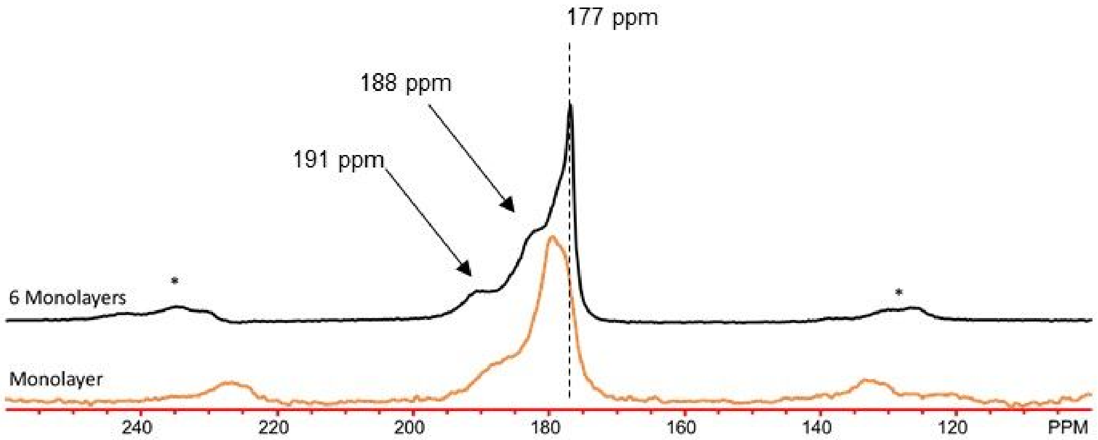

Figure S6. ^{1}H-^{13}C CP MAS NMR spectra of monolayer-adsorbed acetic acid with excess acetic acid on dry TiO_2 (* indicates spinning sidebands).

Using 13C direct polarization can detect all the species formed in the rotor during the operando measurement, shown in Figure S7. All the signals should be consistent and identical to ^{1}H-^{13}C CP MAS NMR except that gas species formed with temperature ramping that cannot be detected by cross polarization technique in Figure 5. As temperature increased to 503 K, products can be easily detected in dry TiO_2 surface, such as acetone peak at 219 ppm, CO_2 peak at 125 ppm and other reaction products between 130-140 ppm. However, in the case of hydrated TiO_2, products are barely detected, further demonstrating the inhibition effect of water on ketonization reaction.

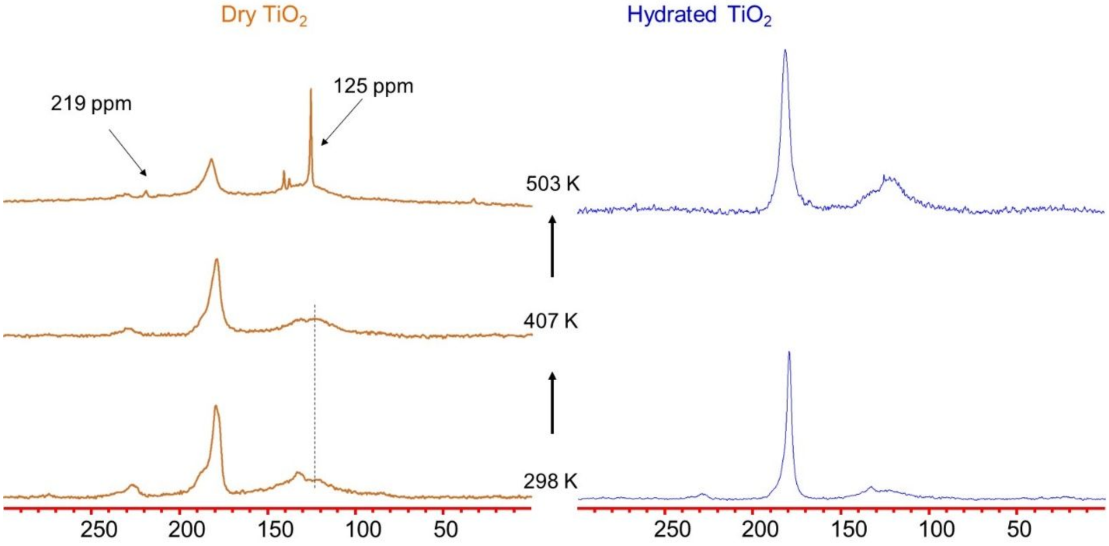

Figure S7. ^{13}C DP MAS NMR spectra of dry and hydrated TiO_2 surfaces saturated by acetic acid at room and elevated temperatures.

S6. Reaction selectivity

Figure S8 shows the carbon selectivity for primary (acetone and CO_2) and secondary (isobutene) products in the acetic acid ketonization on P25 TiO_2 as a function of water pressure at low acetic acid conversions of 3-5%. Isobutene, as the secondary product, only accounts for <10% carbon selectivity. As the water pressure increase, the selectivity of isobutene decreases, indicating water also inhibits the secondary reaction of acetone.

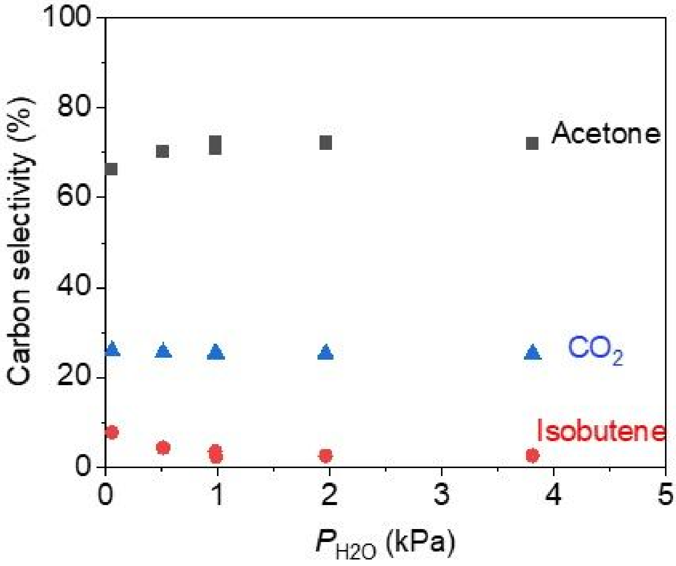

Figure S8. Carbon selectivity of primary and secondary products for the ketonization pathway of acetic acid reaction on TiO_2 as a function of water pressure (543 K, with acetic acid saturated catalyst surface, acetic acid pressure=5-15 kPa)

S7. Reversibility of the water impact

As shown in Figure S9, during the steady state acetic acid ketonization on TiO_2(P25) at 543 K, cofeeding 2kPa of water decreased the rate. When the water cofeeding was stopped after 1h, the reaction rate was fully restored. This confirms that at temperature range of the activity test (<543 K) the presence of H_2O does not induce any phase change

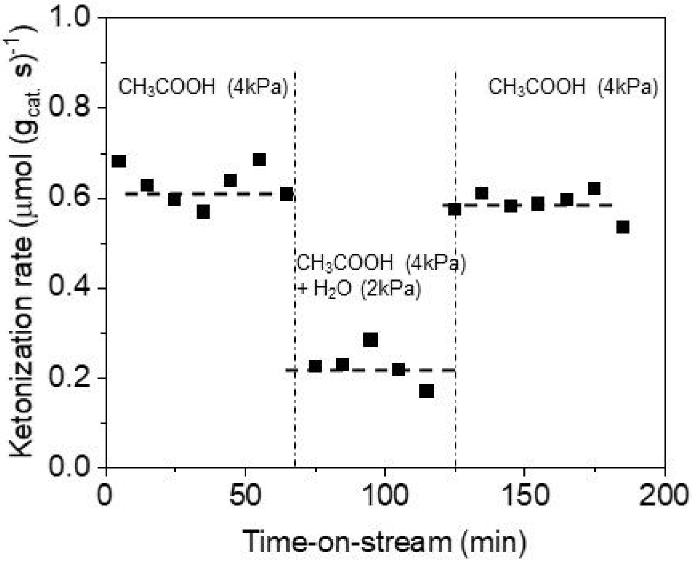

Figure S9. Rate of acetic acid ketonization on TiO_2 as a function of time-on-stream (543 K, 4 kPa acetic acid, 2kPa water)

S8. TPO of spent catalyst

Figure S10 shows the TPO profiles of the spent catalysts (after acetic acid reactions without co-fed H_2O). The major CO_2 formation occurred at around 450-600 K and peaked at around 550 K. Typically, coke combustion has a much higher peak temperature (e.g. 650K-750K for "soft coke" and >800 K for "hard coke") on the non-redox catalysts/supports like TiO_2 [1]and zeolites.[2] Thus the major low-temperature peak (~550 K) of the spent TiO_2 is not associated with coke species. Instead, it is the combustion of acetate intermediates strongly bonded on the spent catalysts. The weak shoulder above 800 K is likely related to a very small amount of coke formation. Together with the stable activity shown in Figure S9, we believe that the catalyst deactivation during the rate measurement is minimal and can be negligible.

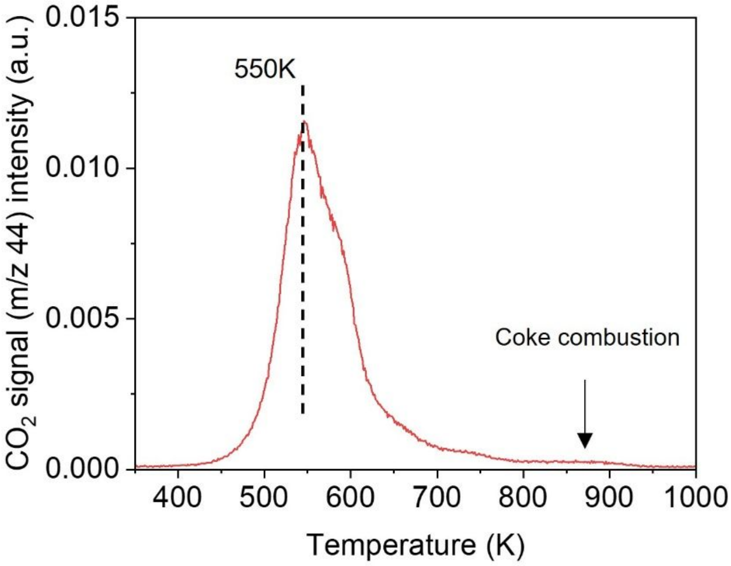

Figure S10. TPO (temperature program oxidation) profiles of spent TiO_2 catalysts after 2h of acetic acid reaction without co-fed H_2O (543 K, 3kPa acetic acid, TOS=2h).

References

1. Guntida, A.; Wannakao, S.; Praserthdam, P.; Panpranot, J., Acidic nanomaterials (TiO_2, ZrO_2, and Al_2O_3) are coke storage components that reduce the deactivation of the Pt–Sn/γ-Al_2O_3 catalyst in propane dehydrogenation. *Catal. Sci. Technol.* **2020,** *10* (15), 5100-5112.
2. Sørensen, M. D. P., The establishment of a coke-burn kinetic model for zeolite catalysts. *Chemical Engineering Science* **2017,** *168*, 465-479.