

Supporting information:

Towards catalytic ketonization of volatile fatty acids extracted from fermented wastewater by adsorption

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Supporting information consist of 4 pages containing 4 tables and 2 figures.

Table S1. Typical composition of fermented wastewater.^{1,2}

Component	Concentration, g/L
Acetic acid	2.5 – 10
Propionic acid	2.5 – 10
Butyric acid	2.5 – 10
Lactic acid	2.5 – 10
Na ⁺	1 – 5
K ⁺	1 – 5
Cl ⁻	1 – 10
H ₂ PO ₄ ⁻ /HPO ₄ ²⁻	1 – 10
SO ₄ ²⁻	1 – 10
S ²⁻	0.3
Mg ²⁺	0.3
Ca ²⁺	0.3
NH ₄ ⁺	0.1
Trace elements (e.g. Co, Ni, Fe ions)	10-4
Inert COD ¹ (e.g. humic acid and fulvic acid)	1

¹ – chemical oxygen demand

Experimental section

Catalyst Preparation

The TiO₂ catalyst was prepared via a sol-gel method with controlled hydrolysis of titanium isopropoxide as reported by Tong et al.³ In a typical synthesis 8 mL of titanium (IV) isopropoxide (Acros, >98%) was dissolved in 24 mL of ethanol (Acros, 99.5%, extra dry). 16 mL of acetic acid (Acros Organics, 99.8%) was added to the mixture dropwise under vigorous magnetic stirring (1200 rpm), followed by addition of 1 mL of H₂SO₄ (95% in water). The solution was kept for 1 h at 40 °C followed by 3 h at 60 °C under continuous mixing. The resulting mixture was transferred to 45 mL autoclave and kept at 120 °C for 13 h under autogenous pressure. The precipitate was separated by a centrifuge and washed thoroughly with distilled water and ethanol. Finally, the catalyst was dried for 12 h at 100 °C followed by calcination at 460 °C in air for 2 h.

The TiO₂/C catalyst was synthesized by modification of a method reported by Pham et al.⁴ The procedure was as follows: activated carbon (SX-2, Norit) was dried at 100 °C for 2 h under vacuum. Titanium (IV) isopropoxide (Acros, >98%) was added dropwise to the dried carbon support to obtain a 30 wt.% loading of TiO₂. The solid was

kept for 2 days at ambient conditions to slowly hydrolyse. Finally, it was dried under vacuum at 100 °C overnight, followed by thermal treatment at 400 °C (5 °C/min) under a nitrogen flow of 50 mL/min.

Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were measured with a Bruker-AXS D2 Phaser X-ray diffractometer using Co-K $\alpha_{1,2}$ radiation ($\lambda = 1.790 \text{ \AA}$). XRD patterns were collected between 20 and 90° 2 θ with an increment of 0.03° (in 2Theta) and an acquisition time of 1 s per step. N₂ physisorption isotherms were recorded to determine surface areas, and pore volumes with a Micromeritics Tristar 3000 setup operating at 77 K. The samples were outgassed prior to performing the measurements for 20 h at 573 K under N₂ flow. Surface areas were determined using the Brunauer–Emmett–Teller (BET) theory, while pore volumes (cm³/g) were determined by the BJH method. Transmission electron microscopy (TEM) images were recorded on the Fei Talos F200X (S) microscope.

Catalyst Testing

The gas-phase ketonization of the VFA mixture was studied in a conventional fixed bed reactor, schematically depicted in **Figure S1a**. The acids mixture consisted of acetic (Acros Organics, 99.8%), propionic (Alfa Aesar, 99%) and butyric (Acros Organics, 99+%) acids with a molar ratio of 1:5.5:19.9, respectively and cyclooctane (Sigma-Aldrich, ≥99%) added as an internal standard. For reactions with water, 60 vol.% of MilliQ water (18.2 M Ω ·cm at 25 °C) was added to the acids mixture with 1,4-dioxane (Sigma Aldrich, ≥99%) used as an internal standard. The liquid feed was pumped by an HPLC pump (LC-20AT, Shimadzu) with a weight hourly space velocity of 3.6 h⁻¹. Mass flow controllers (F-201CV, Bronkhorst) were used to control the flow of N₂ carrier gas (100 mL/min). The borosilicate reactor (i.d. 8 mm) was loaded with TiO₂ catalyst (sieved, to a particle size of 212-150 μ m) mixed with two volumes of silicon carbide. Prior to reaction the catalyst bed was kept at 400 °C for 1 h in N₂ flow (100 mL/min) followed by a reduction in H₂ (50 mL/min). The catalytic studies were performed at atmospheric pressure and temperatures of 375 and 400 °C. The presence of mass transfer limitations was studied by determination of the Weisz-Prater number. The reaction products were analyzed by on-line GC (Bruker, 430-GC) equipped with FID detector and PoraPLOT Q-HT analytical column. Acid conversion, ketone yield and selectivity were calculated using the following equations:

$$\text{Ketone yield} = \frac{2 \times \text{Ketone moles}}{\text{Initial Acid moles}} \times 100\%$$

$$\text{Acid conversion} = \frac{\text{Initial Acid moles} - \text{remaining Acid moles}}{\text{Initial Acid moles}} \times 100\%$$

$$\text{Ketone selectivity} = \frac{2 \times \text{Ketone moles}}{\text{Initial Acid moles} - \text{remaining Acid moles}} \times 100\%$$

The statistical probabilities for the formation of a specific ketone product were calculated based on the mole fractions of corresponding acids, x , where $0 < x < 1$. Then the formation probability for homo-ketone formation is $p_{\text{homo}} = x^2$, while for cross-ketonization the probability is $p_{\text{cross}} = (x_1 \cdot x_2) \cdot 2$.

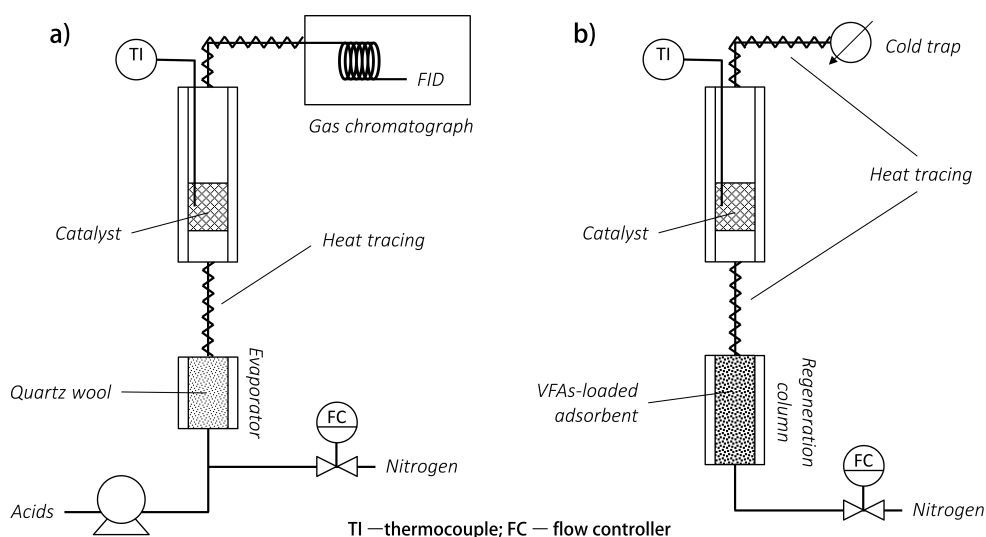


Figure S1 Schematic view of (a) fixed-bed reactor for continuous gas-phase ketonization and (b) fixed-bed reactor for ketonization of VFA adsorbed on a resin batch.

For the ketonization reactions with VFA-saturated resins, the polystyrene-divinylbenzene-based (PS-DVB) adsorbent (Lewatit VP OC 1064 MD PH, Lenntech) was loaded with VFA according to the procedure reported by Reyhanitash et al.² This entailed that for saturation a borosilicate regeneration column (internal diameter of 2.5 cm and column height of 6 cm) was packed with the fresh polymeric adsorbent. Prior saturation, the adsorbent was dried at 120 °C for 3 h under N₂-flow of 200 mL/min. The model solution (Table S3) was pumped through the column (2 mL/min) at room temperature for > 200 min to ensure complete saturation. The integrated recovery/catalytic conversion of VFA was performed in the setup illustrated in **Figure S1b**. The VFA-loaded adsorbent in a borosilicate regeneration column was connected to the gas-phase ketonization reactor. Prior to desorption, the adsorbent was dried under flowing N₂ (200 mL/min) at 70 °C for 1 h. The adsorbent was cooled down to room temperature. Subsequently, the catalyst was dried for 1 h in N₂ flow (100 mL/min) and reduced for 1 h in H₂ (50 mL/min) at 400 °C. The desorption was done at 165 °C under N₂ flow of 100 mL/min. The desorbed gaseous VFA mixture was then led over a fixed bed reactor containing the catalyst and heated to 400 °C. A liquid nitrogen cold trap was used to collect the products. The collected products, diluted in ethanol, were analyzed on a GC-FID (Bruker, 430-GC) equipped with a PoraPLOT Q-HT 25 x 0.32 analytical column and FID-detector, using 1,4-dioxane as an internal standard.

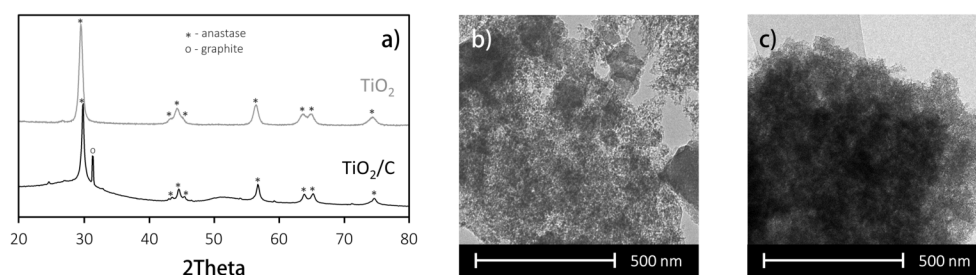


Figure S2 a) XRD patterns of the synthesized catalysts. TEM images of b) activated carbon; c) TiO₂/C.

Table S2 BET surface area and pore volume of the TiO₂ catalysts and the carbon support.

Catalyst	BET surface area, m ² /g	Pore volume, cm ³ /g
TiO ₂	80	0.21
Activated carbon	879	0.84
TiO ₂ /C	622	0.50

Table S3 Composition of the model solution representing fermented wastewater.²

Concentration, wt.%				Concentration, mol/L			pH
Acetic acid	Propionic acid	Butyric acid	Lactic acid	KCl	Na ₂ SO ₄	Na ₂ HPO ₄	
0.25	0.25	0.25	0.25	0.05	0.05	0.1	4.98

Table S4 Composition of VFA mixture on the adsorbent after saturation.²

g/kg of dry adsorbent						
Acetic acid	Propionic acid	Butyric acid	Lactic acid	HCl	H ₂ SO ₄	H ₃ PO ₄
1.5	13.3	60.7	0	0	0	0

References

1. Reyhanitash, E.; Zaalberg, B.; Kersten, S. R. A.; Schuur, B., Extraction of volatile fatty acids from fermented wastewater. *Sep. Purif. Technol.* **2016**, 161, 61–68. DOI: 10.1016/j.seppur.2016.01.037.
2. Reyhanitash, E., Separation of Waste-Derived VFA from Fermented Wastewater. Ph.D. Thesis, The University of Twente, February **2018**.
3. Tong, T.; Zhang, J.; Tian, B.; Chen, F.; He, D., Preparation of Fe³⁺-doped TiO₂ catalysts by controlled hydrolysis of titanium alkoxide and study on their photocatalytic activity for methyl orange degradation, *J. Hazard. Mater.* **2008**, 155, 572–579. DOI: 10.1016/j.jhazmat.2007.11.106.
4. Pham, T. N.; Shi, D.; Sooknoi, T.; Resasco, D. E., Aqueous-phase ketonization of acetic acid over Ru/TiO₂/Carbon catalysts, *J. Catal.* **2012**, 295, 169–178. DOI: 10.1016/j.jcat.2012.08.012.