

Supporting Information

Dehydration of fatty alcohols on zirconia supported tungstate catalysts

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Figures of the results and discussion part

Zirconia supported tungstates

Characterization

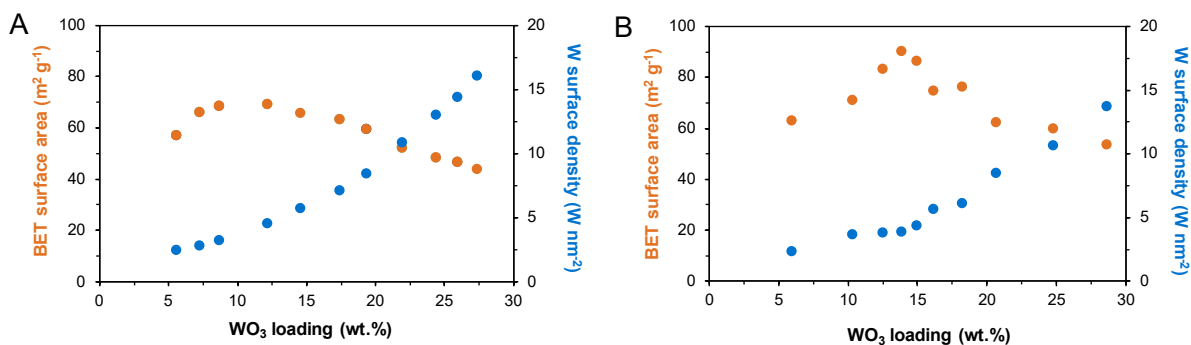


Fig. S1. BET surface area (●) and W surface density (●) as function of the WO_3 loading of different WZrO_2 (A) and WZrOH (B) catalysts.

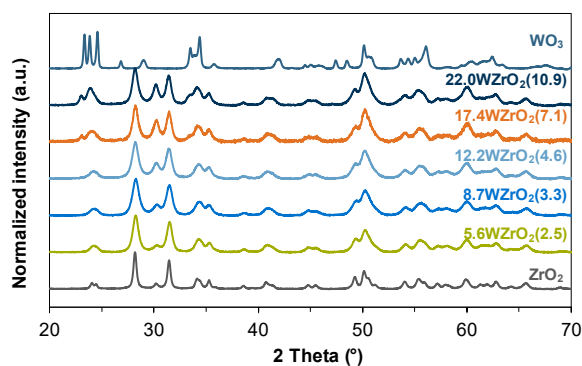


Fig. S2. XRD patterns of the WZrO_2 catalysts with different WO_3 loadings.

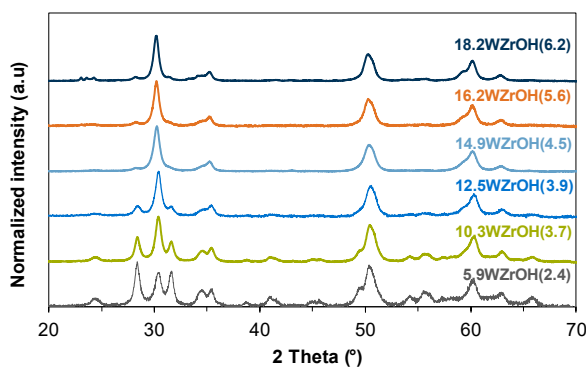


Fig. S3. XRD patterns of the WZrOH catalysts with different WO_3 loadings.

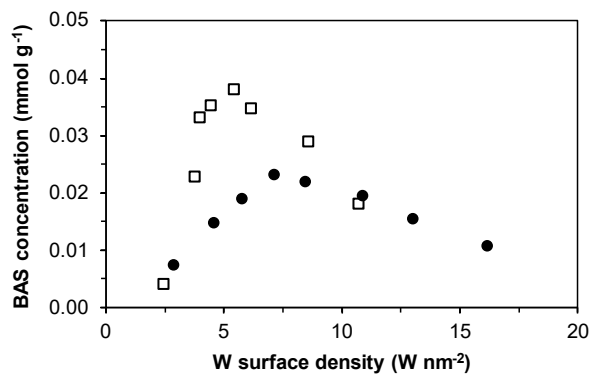


Fig. S4. BAS concentrations as function of the W surface density of different WZrO₂ (●) and WZrOH (□) catalysts.

Octadecanol dehydration over WZrO₂ vs. WZrOH catalysts

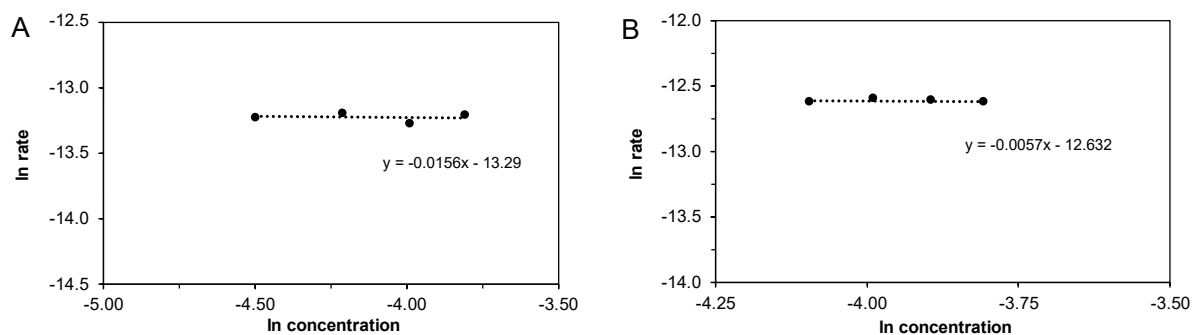


Fig. S5. Rate dependency on the octadecanol concentration over the 14.6WZrO₂(5.7) (A) and 12.5WZrOH(3.9) (B) catalysts. Reaction conditions: catalyst (0.2 g), decalin (100 mL), 180°C, $p(\text{H}_2) = 40$ bar, 700 rpm.

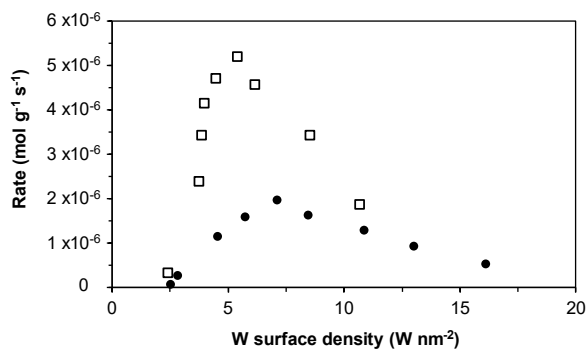


Fig. S6. Rate of the octadecanol dehydration as function of the W surface density on different WZrO₂ (●) and WZrOH (□) catalysts. Reaction conditions: catalyst (0.2 g), octadecanol (0.5 g), decalin (100 mL), 180°C, $p(\text{H}_2) = 40$ bar, 700 rpm.

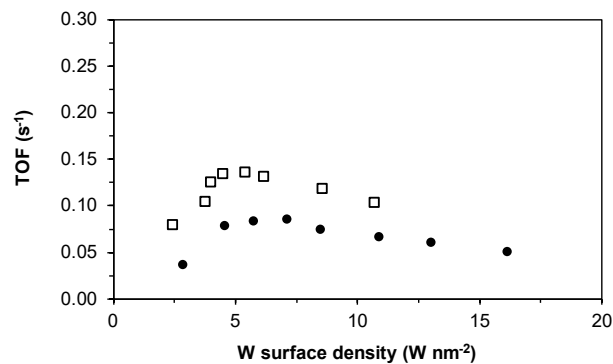


Fig. S7. TOF of the octadecanol dehydration as function of the W surface density on different WZrO₂ (●) and WZrOH (□) catalysts. Reaction conditions: catalyst (0.2 g), octadecanol (0.5 g), decalin (100 mL), 180°C, $p(\text{H}_2) = 40$ bar, 700 rpm.

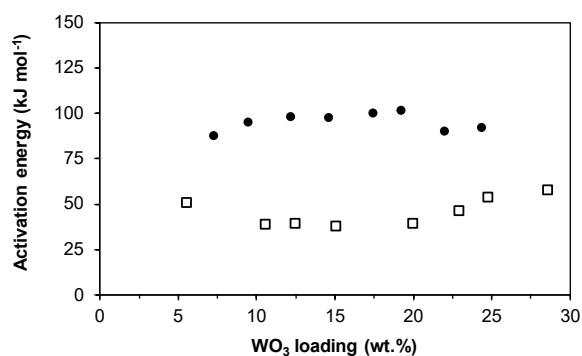


Fig. S8. Activation energy of the octadecanol dehydration as function of the WO₃ loading on different WZrO₂ (●) and WZrOH (□) catalysts.

Promotion effect of platinum

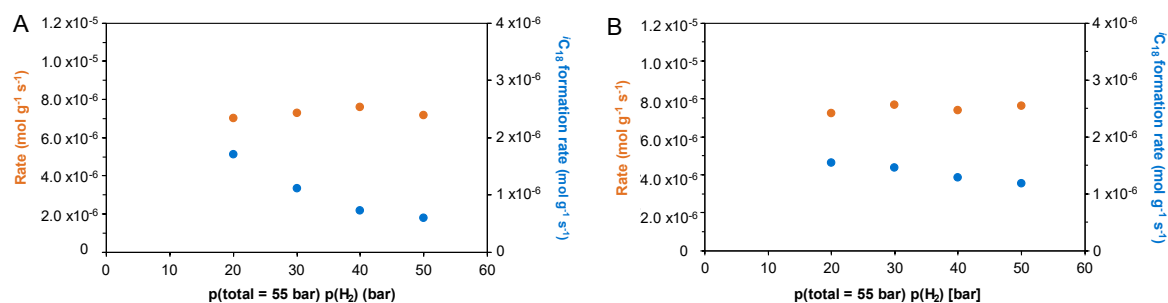


Fig. S9. Rate of the octadecanol dehydration (●) and the *iso*-octadecane formation (●) over the 1Pt14.9WZrOH(4.5) (A) and 0.5Pt14.9WZrOH(4.5) (B) catalyst at different H₂ pressures and constant total pressure.

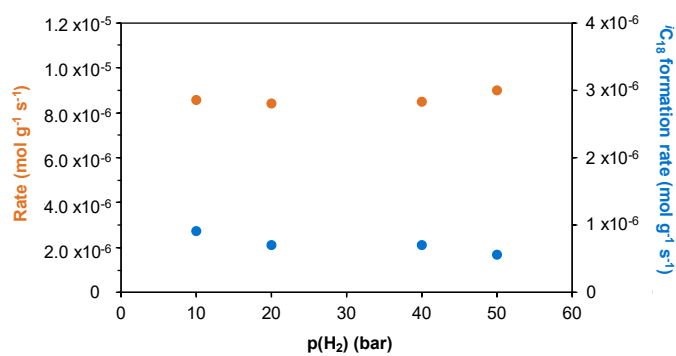


Fig. S10. Rate of the octadecanol dehydration (●) and the *iso*-octadecane formation (●) as function of the H_2 pressure over the 1Pt14.9WZrOH(4.5) catalyst.

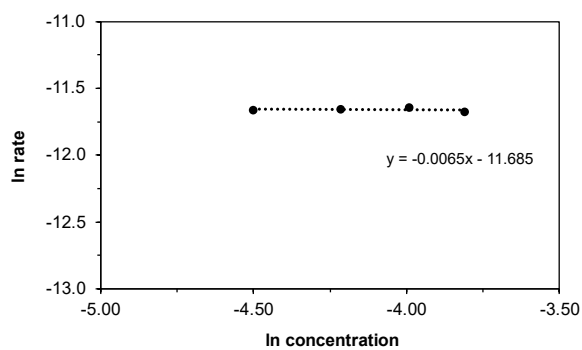


Fig. S11. Rate dependency on the octadecanol concentration over the 0.5Pt16.2WZrOH(5.4) catalyst. Reaction conditions: catalyst (0.1 g), decalin (100 mL), 180°C, $p(\text{H}_2)$ = 40 bar, 700 rpm.

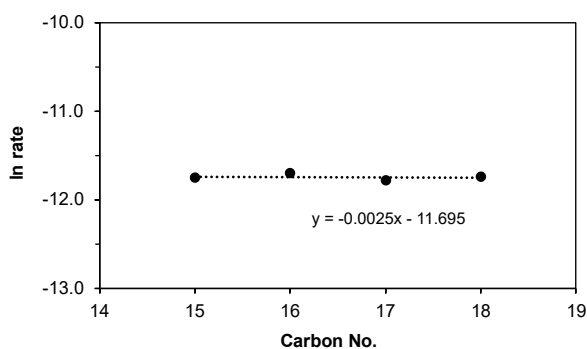


Fig. S12. Rate dependency on the carbon chain length over the 1Pt14.9WZrOH(4.5) catalyst. Reaction conditions: catalyst (0.1 g), decalin (100 mL), 180°C, $p(\text{H}_2)$ = 40 bar, 700 rpm.

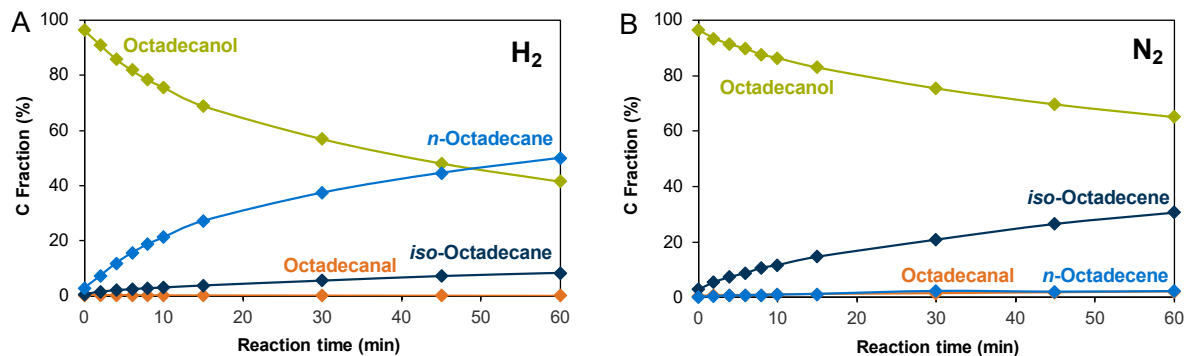


Fig. S13. Product distribution of the octadecanol dehydration over the 0.5Pt20.6WZrOH(8.6) catalyst in H₂ (A) and N₂ (B) atmosphere. Reaction conditions: catalyst (0.1 g), octadecanol (0.5 g), decalin (100 mL), 180°C, $p(\text{H}_2/\text{N}_2) = 40$ bar, 700 rpm.

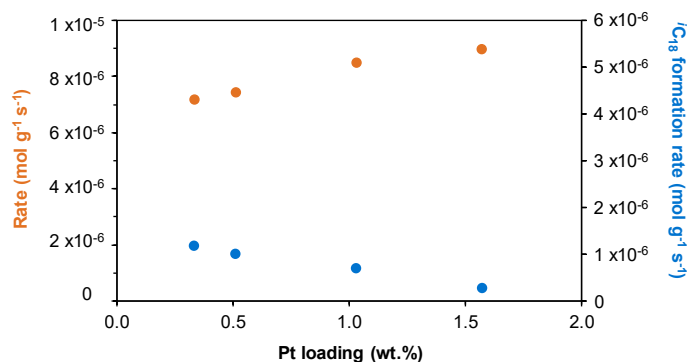


Fig. S14. Rate of the octadecanol dehydration (●) and the *iso*-octadecane formation (●) as function of the Pt loading over Pt14.9WZrOH(4.5) catalysts.

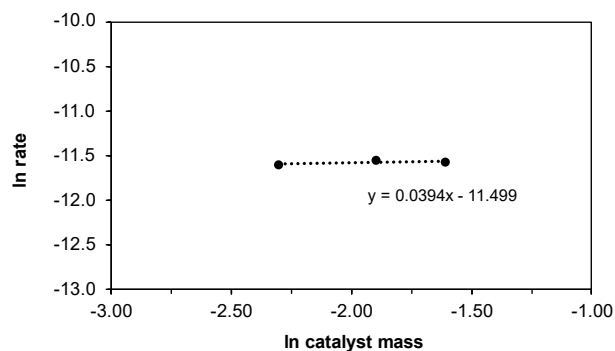
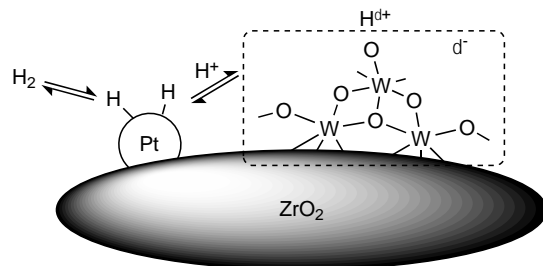


Fig. S15. Rate dependency on the catalyst mass over the 0.5Pt16.2WZrOH(5.4) catalyst. Reaction conditions: octadecanol (0.5 g), decalin (100 mL), 180°C, $p(\text{H}_2) = 40$ bar, 700 rpm.



Scheme S1. The platinum-facilitated adsorption of hydrogen enables a partial reduction of the tungstates already at intermediate temperatures (Scheme adopted from Barton et al.¹).

Note S1. The promotion effect of platinum addition on a crystalline ZrO₂ support was also tested and showed a similar rate enhancement as the amorphous ZrOH support, e.g., ~51% increase from $4.5 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$ to $9.1 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$ with 0.5Pt17.4WZrO₂(7.1) at 200°C reaction temperature.

Aqueous phase

As the microalgae are cultivated in an aqueous environment, the tungstated zirconia catalyzed octadecanol dehydration was also tested in water. However, no conversion could be observed. It is hypothesized that the apolar substrate is not in contact with the polar catalyst surface, which is blocked by the surrounding water. Thus, a more apolar character of the tungstate catalyst was implemented by choosing activated carbon as the support.

Interestingly, the dehydration of octadecanol with activated carbon supported tungstate catalysts (WC) shows high activity in both organic and aqueous phase with a similar product distribution (Fig. S16 A and B).

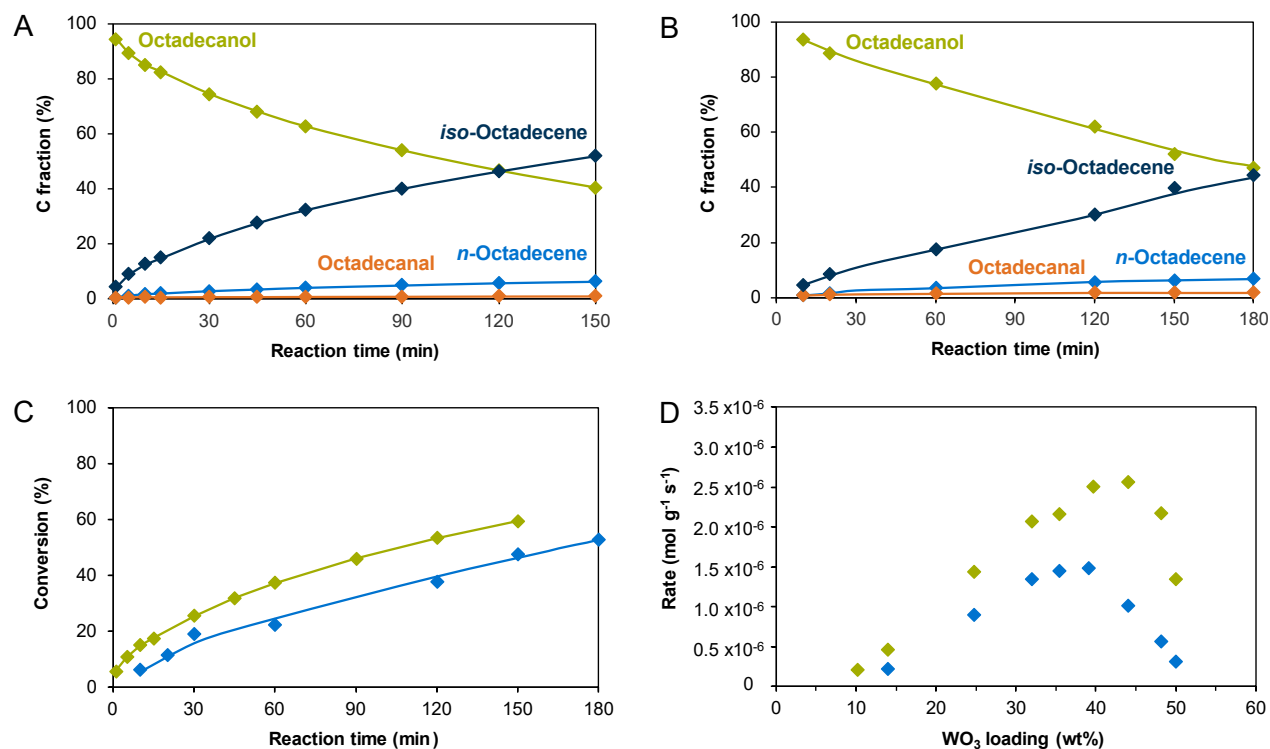


Fig. S16. Product distribution of the octadecanol dehydration over the 25WC(1.4) catalyst in organic (A) and in aqueous (B) phase. Conversion (C) and rate as function of the WO₃ loading (D) of the octadecanol dehydration over the 25WC(1.4) catalyst in organic (♦) and aqueous (◆) phase. Reaction conditions: catalyst (0.20 g), octadecanol (0.45 g), solvent (100 mL), 240°C, $p(\text{H}_2) = 40$ bar, 700 rpm.

The reaction order in octadecanol was determined to be zero in water and one in decalin. This can be interpreted as that the apolar substrate is stronger bonded to the carbon support in water due to its higher driving force towards the catalyst surface than in an apolar surrounding. Thus, the high octadecanol surface coverage of the catalyst in aqueous phase is causing a substrate independent reaction whereas the lower surface coverage in the organic solvent is leading to a first order rate dependency. As a consequence, even though the initial rate in decalin is higher than in water, the conversion is similar for both solvents, especially with increasing reaction time which can be seen in Fig. S16 C.

Significantly, in Fig. S16 D the rate dependency of the octadecanol dehydration on the tungsten loading in aqueous (◆) and organic (♦) phase shows once more a volcano-shaped relationship

with a maximum above monolayer coverage. In water the highest rate was measured on the 39WC(2.3) catalyst with $1.5 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$, while the fastest conversion in decalin was obtained over the 44WC(2.6) catalyst with $2.6 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$. This implies that also for the activated carbon supported catalysts a more active species exists next to the isolated and polymeric mono-oxo $\text{W}=\text{O}$, and the m-WO_3 nanoparticles.

References

1. D. G. Barton, S. L. Soled, G. D. Meitzner, G. A. Fuentes and E. Iglesia, *J. Catal.*, 1999, **181**, 57-72.