BRC Science Highlight
March 2021

Reactive Species and Reaction Pathways for the Oxidative Cleavage of 4-Octene and Oleic Acid with H2O2 over Tungsten Oxide Catalysts

Background/objective

The oxidative cleavage of bio-based unsaturated fatty acids (UFA) with H_2O_2 offers pathways to create unique and valuable monomers (e.g., C9 diacids), which are difficult to obtain from petroleum-based precursors. Solid tungsten oxides facilitate this chemistry, but the mechanism and identity of reactive species over these solid catalysts remain debated. Here, we reveal the H_2O_2-derived intermediates and the reaction mechanism by which 4-octene and oleic acid undergo oxidative cleavage to compare kinetics and active site structures of γ-Al_2O_3 supported tungstates (WO_x-Al_2O_3) and WO_3 nanoparticles.

Approach

- Synthesized WO_x-Al_2O_3 catalysts with increasing W content to introduce isolated WO_x species on γ-Al_2O_3. WO_3 nanoparticles were obtained commercially.
- Examined surface WO_x structure and H_2O_2-derived reactive intermediates of WO_x-Al_2O_3 and WO_3 nanoparticles by spectroscopic techniques.
- Measured rates of reactant, oxidant, and intermediate concentrations to propose oxidative cleavage mechanism and determine kinetically relevant step.
- Examined activation enthalpy for oxidative cleavage and adsorption enthalpy of epoxide over WO_x-Al_2O_3 and WO_3 nanoparticles to reveal reasons of different catalytic activity of WO_x and WO_3 sites.

Results

- Identified the W-peroxo (W-(η^2-O_2)) that are reactive intermediates for producing aldehydes and acids.
- Demonstrated that the oxidative cleavage mechanisms on the isolated WO_x sites and on WO_3 nanoparticles are similar.
- Revealed that WO_x-Al_2O_3 catalysts stabilize kinetically relevant transition states more effectively, and therefore, show greater rates and selectivity for oxidative cleavage than WO_3 nanoparticles.

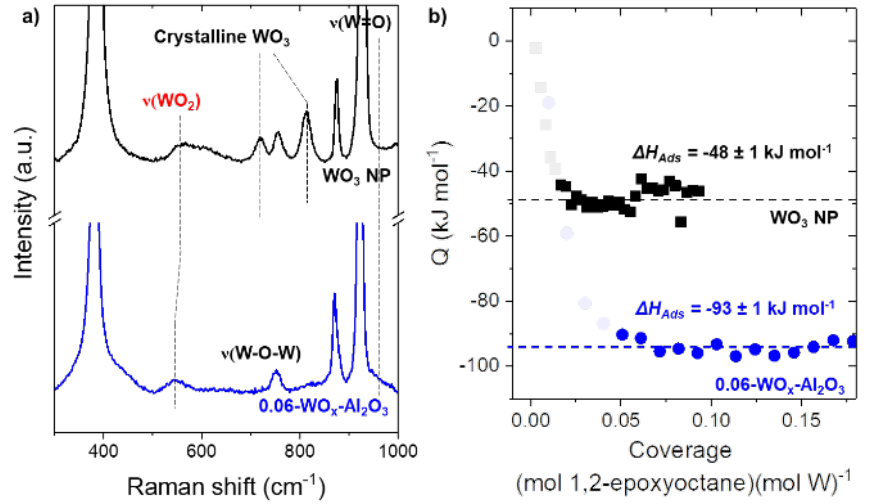

Figure. a) *In situ* Raman spectra of WO_x-Al_2O_3 (—) and WO_3 (—) in flowing CH_3CN (0.5 M H_2O_2, 1.98 M H_2O, 313 K, 1 $cm^3 \cdot min^{-1}$) and b) adsorption enthalpies for 1,2-epoxyoctane on WO_x-Al_2O_3 (●) and WO_3 (■) in CH_3CN at 298 K as a function of 1,2-epoxyoctane coverage.

Significance

WO_x-Al_2O_3 catalysts are effective for oxidative cleavage reactions due to high rates and selectivity for oxidative cleavage products, and there are significant opportunities to further improve the performance of solid catalysts to obtain valuable products from bio-based fatty acids via oxidative cleavage with H_2O_2.

*Yun, D., et al., 2021. "Reactive Species and Reaction Pathways for the Oxidative Cleavage of 4-Octene and Oleic Acid with H2O2 over Tungsten Oxide Catalysts." **ACS Catalysis** 2021, 11: 3137–3152. DOI: 10.1021/acscatal.0c05393.*

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