Purification of Alkene Stereoisomers through Z-Selective Ethenolysis

**Significance:** Many methods exist for preparing disubstituted E-olefins, such as the Horner–Wadsworth–Emmons reaction and olefin cross-metathesis. While these reactions have proven to be highly reliable and practical, the undesired Z-isomer is often difficult to separate by chromatography or distillation. In the present communication, the authors disclose how pure E-olefins can be obtained from an E/Z mixture through the selective ethenolysis of the Z-isomer.

**Comment:** The by-products of the reaction are of much lower molecular weight than the starting materials, so the pure E-isomer can often be obtained through distillation. The rate of ethenolysis is found to be up to 30 times faster for the Z-isomer, explaining why such a highly pure E-olefin can be obtained. The scale of the reactions was not mentioned.

**Selected examples:**

\[ \text{Mo catalyst (0.2–2 mol%)} \]
\[ \text{ethylene (4–20 atm)} \]
\[ \text{PhH or no solvent} \]
\[ \text{r.t., 15 min to 18 h} \]
\[ \text{E/Z mixture} \]

\[ \text{E-isomer + ethenolysis products from Z-isomer} \]

**Two-step synthesis of pure E-olefins:**

\[ \text{Mo catalyst (4 mol%)} \]
\[ \text{16 h} \]
\[ \text{E/Z = 4:1} \]

\[ \text{Mo catalyst (2 mol%)} \]
\[ \text{ethylene (4 atm)} \]
\[ \text{2 h} \]

\[ \text{pure E-isomer 67% overall yield} \]

\[ \text{E/Z = 4:1 thermodynamic mixture} \]