

**Chem 91/131 2007 Problem Set 10**  
**(Topics: heterogeneous catalysis) (25 pts)**

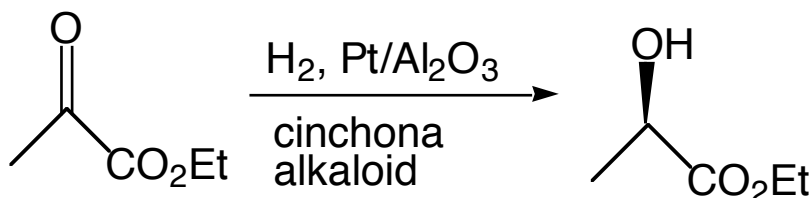
1. (9 pts, 4+3+2) Maitlis has used doubly  $^{13}\text{C}$ -labeled vinyl halides as probes of the mechanism of the Fischer-Tropsch reaction (see *Appl. Catal. A: General* **1999**, *186*, 363-374, link on the webpage).

(a) Summarize the new mechanism proposed for the Fischer-Tropsch reaction, and the evidence for it in comparison to other proposals.

(b) Give an example of the design, analysis, and interpretation of an experiment with a  $^{13}\text{C}$ -labeled probe molecule.

(c) Critically evaluate the proposed mechanism. Do you believe it? Why or why not?

2. (4 pts) Blaser et al. at Ciba-Geigy developed catalytic asymmetric hydrogenation of  $\alpha$ -ketoesters using a heterogeneous Pt catalyst. The following observations were made.



(a) Alkaloid-modified surfaces were up to 100 times more active than ligand-free surfaces.

(b) Only catalytic amounts of the alkaloid were required to give high ee.

(c) No correlation was found between ee and total or metal surface area.

(1) Propose a mechanism for the asymmetric hydrogenation.

(2) This is a *heterogeneous* example of ligand-accelerated catalysis. What features of it are similar, and which are different, from the homogeneous examples covered in class?

3. (4 pts) The hydrogenation of 2-butyne on  $\text{Pd}/\text{Al}_2\text{O}_3$  at 0-25  $^\circ\text{C}$  gives mainly cis-2-butene, although the trans form is more stable. The reaction is zero order in acetylene and first order in hydrogen. As long as unreacted acetylene remains, the cis-2-butene does not react further. If deuterium is used instead of hydrogen, the product is 2,3-dideuterio-cis-2-butene.

Suggest a mechanism for the hydrogenation which is consistent with these observations.

4. (4 pts) Silver powder was covered with a layer of chemisorbed  $^{16}\text{O}_2$ , and then treated with a mixture of ethylene and  $^{18}\text{O}_2$ . The experiment was done under conditions in which gas-phase  $^{18}\text{O}_2/^{16}\text{O}_2$  exchange was slow.

Initially the ethylene oxide formed is enriched in  $^{16}\text{O}$ . After some time the two oxygen isotopes are incorporated into the product at about the same rate.

Carbon dioxide formed by complete oxidation of ethylene undergoes rapid O scrambling.

Suggest a mechanism for the epoxidation which is consistent with these observations.

5. (4 pts) Several silica-supported transition-metal catalysts (Ni, Co and Ru) were covered with  $^{13}\text{C}$ -labelled carbon, deposited by disproportionation of  $^{13}\text{CO}$  (this is called the Boudouard reaction). Subsequent exposure of these catalysts to  $^{12}\text{CO}$  and  $\text{H}_2$  gave  $^{13}\text{CH}_4$  and a mixture of hydrocarbons containing several  $^{13}\text{C}$  atoms within one molecule.

Suggest a mechanism which explains these results.

What control experiments might be necessary for this experiment?