

Chem 91/131 Problem Set 9
(Topics: heterogeneous catalysis) (25 pts)

1. (4 pts, 1+3) On Fe(100) MeCl chemisorbs dissociatively to form adsorbed methyl groups. These react further to give hydrogen and surface carbide.
(a) Give an example of a related reaction of an alkyl halide with a metal complex in solution to give a metal-alkyl complex.
(b) Suggest a mechanism for the decomposition of the surface methyl groups.

2. (6 pts, 2 each) Addition of ethylene to a hydrogen-saturated Fe(100) surface gives adsorbed ethyl groups. Explain the following observations about this system by suggesting mechanisms for the reactions, making comparisons to solution chemistry where appropriate:
(a) Addition of ethylene to a deuterated surface Fe(100)-D gives a range of deuterated ethylenes (up to 4 D per ethylene)
(b) The rate of β -elimination of Fe-C₂H₅ is faster than in Fe-C₂D₅-- $k_H/k_D = 4.9$.
(c) Ethane is not formed spontaneously, but addition of CO to Fe-Et gives ethane at 165 K. Coadsorption of CO and ethylene on Fe....H also gives ethane but only at the higher temperature of 170 K.

3. (5 pts, 1 each) On palladium surfaces, acetylene undergoes 5 competing reactions:
(a) reversible desorption
(b) reversible C-H bond scission
(c) decomposition to carbon and hydrogen
(d) hydrogenation to ethylene (no H₂ added!)
(e) trimerization to benzene

Suggest mechanisms for these reactions, using analogy with soluble transition metal complexes if needed.

4. (5 pts) Several group 8 metals catalyze the hydrogenolysis of cyclopropanes at room temperature. This reaction with 2,2-dimethylcyclopropane gives neopentane. When deuterium is used, the neopentane formed is Me₂C(CH₂D)₂. Suggest a mechanism for this reaction.

5. (5 pts) On ZnO at 300 °C, ¹³C¹⁶O and ¹²C¹⁸O undergo isotope mixing to form ¹³C¹⁸O and ¹²C¹⁶O. Suggest a mechanism for this reaction.