Practical Catalytic Heterogenous Hydrogenation

Reference: *Practical Catalytic Hydrogenation, Techniques and Applications* by Morris Freifelder, Wiley-Interscience 1971. Below is a reproduction of the table of contents from this book (out of print, but copies can still be found on Amazon.com). The topics covered will follow the same organization.

Course Outline.

I. Introduction
II. Factors in Hydrogenation
III. Catalysts and their applications
    A. Rhenium
    B. Ruthenium
    C. Copper Chromium Oxide
    D. Cobalt
    E. Nickel
    F. Platinum
    G. Palladium
    H. Rhodium
    I. Metal sulfides and sulfactive catalysts
    J. Mixed Noble Metal Catalysts
IV. Catalyst inhibitors and poisons
    A. Metals and Metal Salts
    B. Halogen-containing compounds
    C. The effect of nitrites
    D. Compounds containing Arsenic Antimony, Oxygen, Phosphorous, Selenium, and Tellurium
    E. The effect of Sulfur
    F. The effect of the nitrogen atom
    G. Other inhibitors
    H. Practical Use of Catalyst Poisons

V. Catalyst Promoters
    A. Metallic and non-metallic Substances
    B. The effect of Oxygen
    C. The effect of Noble metals on Nickel Catalysts
    D. The Effect of acids
    E. The Effect of water

VI. Other Effects in Hydrogenation
    A. Solvents
    B. The Hydrogen Acceptor
    C. Agitation
    D. Catalyst supports

VII. Procedures
    A. Equipment
    B. Reaction conditions
    C. Choice and amount of catalyst
    D. Addition of Catalyst
    E. Safety in Operation
    F. Economics

VIII. Acetylenes
- A. Reductions with Platinum catalyst
- B. Reductions with Nickel catalyst
- C. Reductions with Palladium catalyst
  1. Reduction with deactivated Palladium catalyst
- D. Use of Iron catalyst
- E. Selective hydrogenation in the presence of other Reducible Groups
  1. Reduction in the presence of another acetylenic bond
  2. Reduction in the presence of other olefinic bonds
  3. Reduction in the presence of Aldehyde and Ketone Groupings
  4. Reduction in the presence of Halogen
  5. Reduction in the presence of nitro groups
  6. Steric effects

IX. Olefins
- A. Variables affecting the Hydrogenation of Olefins
- B. Mono-enes
- C. Di- and polyenes
- D. Selective Hydrogenation in the presence of other reducible groups
  1. Aldehydes and ketones
  2. Conjugated Dienones
  3. Selective reductions in the presence of unsaturated nitrogen-containing groups
  4. Selective reductions in the presence of hydrogenolyzable functions.

X. Reduction of the nitro group
- A. In Benzenoid compounds
  1. Conditions and Influences on reduction
  2. Nitrophenols
  3. Nitrobenzoic and nitrophenylalkanoic acids
  4. Aromatic nitro compounds with basic side chains
  5. Aromatic polynitro compounds
  6. Polyaromatic nitro compounds
  7. Nitrophenylarsonic, boronic, and phosphonic acids, and related compounds
  8. Partial reduction
- B. In Heterocyclic compounds
- C. Selective reduction in compounds containing other reducible groups
  1. Olefinic bonds
  2. Aldehydes and ketones
  3. Unsaturated Nitrogen-containing groups
  4. In non-aromatic compounds

5. In N-nitro compounds

XI. Reduction of the Nitroso, Azo, and Azoxy groups
- A. Nitroso group
- B. Azo and azoxy groups
- C. Other N=N systems

XII. Nitriles
- A. Control of Secondary amine
- B. Aliphatic and aromatic mononitriles
- C. Cyano acids and esters
- D. Aminonitriles
- E. Cyanohydrins
- F. Dinitriles
- G. Aldehydes from nitriles
- H. Secondary and tertiary amines from reduction of nitriles
- I. Selective Reductions
  1. In the presence of Aromatic Rings
  2. In the presence of non-aromatic Rings
  3. In the Presence of ketones
  4. In the presence of reducable Nitrogen-Containing groups
  5. In the presence of Hydrogenolyzable groups

XIII. Reduction of Oximes
- A. Reaction conditions and Catalysts
  1. Cobalt
  2. Nickel
  3. Platinum
  4. Palladium
  5. Ruthenium and Rhodium
- B. Oximino Acids, Esters, and Amides
- C. Indanone Oximes
- D. Dioximes
- E. Amidoximes to Amidines
- F. Partial Reduction
- G. Reduction in the presence of other functions
  1. Cyano groups
  2. Ketones
  3. Hydrogenolyzable groups

XIV. Carbonyl Groups
- A. Aldehydes
- B. Monoketones
- C. Diketones
- D. Carbonyl to methylene
- E. Selective hydrogenation of the carbonyl group
    1. In Aromatic Ring Systems
    2. In the Presence of Functional Groups
    3. In the Presence of Hydrogenolyzable Groups

XV. Reduction of the C=N Bond
- A. Primary Imines
- B. N-Substituted Imines
- C. The unconjugated C=N bond in Heterocycles
- D. The C=N bond in Azines, Hydrazones, and Semicarbazones
- E. In amidines
- F. Selective Hydrogenations
    1. In the Presence of an Olefinic Bond
    2. In the Presence of a Carboxyl Group
    3. In the Presence of a Cyano Group
    4. In the Presence of Hydrogenolyzable groups

XVI. Reductive amination
- A. Aldehydes
    1. Catalysts
- B. Ketones
    1. Nickel-catalysed Reactions
    2. Reductions over noble metals
    3. Effect of Acidic Agents
- C. Selective Hydrogenations
    1. In the Presence of Olefinic Bonds
    2. In the Presence of Halogen

XVII. Reductive Alkylation
- A. Procedures
- B. Catalysts
- C. Secondary amine from primary amine
    1. Alkylation with Aldehydes
    2. Alkylation with Ketones
    3. Formation of Teriary amine
    4. Selective Hydrogenation

XVIII. Hydrogenolysis of Allylic Oxygen and Nitrogen containing compounds
    A. Allylic Oxygen Compounds
    B. Allylic nitrogen compounds
    C. Selective Reductions
        1. Between O- and N- allyl groups
        2. In the presence of functional groups

XIX. Debenzylation and Related reactions
XX. Dehalogenation
XXI. Hydrogenolysis of Carboxyl-containing Groups
XXII. Hydrogenolysis of Alcohols, Ethers, Acetals, and Ketals
XXIII. Miscellaneous Hydrogenations
XXIV. Aromatic Ring Systems
XXV. Hydrogenation of Sulfur-Containing Compounds