

Industrial Catalysis
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Course Outline

- 1. Introduction to Industrial Catalysis (Weeks 1 & 2)**
 - 1.1. Historical background
 - 1.1.1. Early Catalyst Examples
 - 1.1.2. Highlights of Catalysis Technology
 - 1.2. Catalyst Definitions
 - 1.3. Kinetics and Catalysis
 - 1.4. Thermodynamics
 - 1.5. Key Concepts: Activity, Selectivity, Efficiency/turnover, Life
 - 1.5.1. Activity: Batch Measures
 - 1.5.2. Activity: Space Velocity
 - 1.5.3. Space Velocity Examples
 - 1.5.4. Activity: Turnover Rate
 - 1.5.5. Turnover Example
 - 1.5.6. Selectivity
 - 1.5.7. Selectivity Example 1
 - 1.5.8. Selectivity Example 2
 - 1.5.9. Catalyst Life
 - 1.6. Catalytic Mechanism
 - 1.6.1. Representing Mechanisms: Electron Pushing
 - 1.6.2. Representing Mechanisms: Name Reaction Examples
 - 1.6.3. Elementary Catalytic Reaction Steps
 - 1.6.4. Representing Catalytic Mechanisms: Tollman Formalism
 - 1.6.5. Catalytic Mechanism Example: Hydroformylation of Olefins
 - 1.7. Homogeneous vs. Heterogeneous Catalysis
 - 1.7.1. Homogeneous Example: Epoxidation of Propylene
 - 1.7.2. Heterogeneous Example: Oxidation of Propylene to Acrolein
 - 1.7.3. Advantages of Homogeneous Catalysis
 - 1.7.4. Advantages of Heterogeneous Catalysis
 - 1.8. Major reaction types
 - Acid Catalysis
 - Oxidative Processes
 - Reductive Processes
 - Polymerization
 - Environmental
 - 1.8.1. Industrial Examples
- 2. Acid Catalysis (Weeks 3 & 4)**
 - 2.1. Basic Concepts
 - 2.1.1. Acid Catalyst Periodic Table
 - 2.1.2. pKa Acidity Scale
 - 2.1.3. Ho Acidity Scale for Superacids
 - 2.1.4. Solid Superacid Example” Phosphotungstic Acid

- 2.1.5. Bronsted vs. Lewis Acidity
- 2.1.6. Some Common Solid Acid Catalysts
- 2.1.7. Silica-Alumina Solid Acids
- 2.1.8. Zeolite Synthesis
- 2.1.9. Zeolite Acid Sites
- 2.1.10. Bronsted and Lewis Acidity Measurements in Solids
- 2.1.11. Mechanism of Acid Catalyzed Reactions
- 2.1.12. Thermodynamics
- 2.2. Elements of Catalyst Design
 - 2.2.1. Active Site Distribution
 - 2.2.2. Zeolites
 - 2.2.3. Other Silica-Alumina Frameworks
 - 2.2.4. Shape Selectivity
 - 2.2.5. Surface Activity Effects
 - 2.2.6. Surface Activity – Small Crystallite Example
 - 2.2.7. Heat Treatment
 - 2.2.8. Common Catalyst Supports
 - 2.2.9. Catalyst Supports: Hydrophobic vs. Hydrophilic Surfaces
- 2.3. Major Industrial Processes – Refinery
 - 2.3.1. Hydrocarbon Cracking (Fluid Cat Cracking)
 - 2.3.2. Disproportionation of Aromatics
 - 2.3.3. Paraffin Isomerization
 - 2.3.4. Alkylation
 - 2.3.5. Methanol to gasoline (MTG) Process
 - 2.3.6. MTBE Synthesis - Etherification
- 2.4. Major Industrial Processes – Chemical
 - 2.4.1. Benzene Ethylation - Ethylbenzene
 - 2.4.2. Cumene
 - 2.4.3. Beckman Isomerization - Caprolactam
 - 2.4.4. Esterification
- 2.5. Trends in Acid Catalysts

Test – Chapters 1 & 2

3. Oxidation Catalysis (Weeks 5 & 6)

- 3.1. Concepts
 - 3.1.1. Oxidation Catalyst Periodic Table
 - 3.1.2. Oxidation Thermodynamics
 - 3.1.3. Recognizing Organic Oxidation States
 - 3.1.4. Oxidation Catalysis Concepts – Homogeneous
 - 3.1.5. Oxidation Catalysis Concepts – Heterogeneous
 - 3.1.6. Elementary Reaction Steps
 - 3.1.7. Mechanisms – Homogeneous Molecular
 - 3.1.8. Mechanisms – Heterogeneous Surface
 - 3.1.9. Mechanisms – Heterogeneous Bulk
- 3.2. Elements of Catalyst Design

- 3.2.1. Metal substitution
- 3.2.2. Active Site Isolation
- 3.2.3. Surface vs. bulk composition
- 3.2.4. Promoters
- 3.2.5. Oxidation Catalyst Synthesis
- 3.3. Major Industrial Processes
 - 3.3.1. Epoxidation / Styrene Monomer/Propylene Oxide (SMPO)
 - 3.3.2. Allylic Oxidation / Acrylonitrile
 - 3.3.3. Vinyl Acetate / Wacker Oxidation
 - 3.3.4. Cyclohexanol/one – Cyclohexane Oxidation
 - 3.3.5. Adipic Acid / Nylon 6,6
 - 3.3.6. Maleic Anhydride - Paraffin Oxidation
 - 3.3.7. Aromatic oxidation / Terphthalic Acid
 - 3.3.8. Aromatic oxidation / Phthalic Anhydride
 - 3.3.9. Aromatic oxidation / Cumene to Phenol/Acetone

4. Polymerization Catalysis (Weeks 7 & 8)

- 4.1. Concepts
 - 4.1.1. Polymerization Catalyst Periodic Table
 - 4.1.2. Thermodynamics
 - 4.1.3. Molecular Weight: Mn, Mw, and Polydispersity
 - 4.1.4. Polymerization Reaction Mechanisms
 - 4.1.5. Polymerization Mechanisms: Elementary Steps
 - 4.1.6. Anionic Polymerization / Polybutadiene
 - 4.1.7. Cationic Polymerization / Styrene
 - 4.1.8. Metal Oxide/Coordination Catalyst Polymerization / Polyolefins
 - 4.1.9. Coordination: Ziegler-Natta
 - 4.1.10. Coordination: Metallocene
 - 4.1.11. Free Radical Polymerization / Polystyrene
 - 4.1.12. Living Polymerization / Polyacrylates
- 4.2. Elements of Catalyst Design
 - 4.2.1. Metal substitution: Propylene Isomers
 - 4.2.2. V-Based Polypropylene Catalysts: Syndiotactic
 - 4.2.3. Ti-Based Polypropylene Catalysts: Isotactic
 - 4.2.4. Ligand Effect: Constrained Geometries
 - 4.2.5. Isotactic from CP* Catalysts
 - 4.2.6. Non-Coordinating Anion Activation
 - 4.2.7. Effect of Solvents: Butadiene (BD)
 - 4.2.8. Catalyst Synthesis: Particle Microreactor
 - 4.2.9. Single vs. Multiple Sites Polyolefin Catalysts
- 4.3. Major Industrial Processes
 - 4.3.1. - Polyethylene and Isotactic Polypropylene: $\text{TiCl}_4/\text{AlEt}_2\text{Cl}_2/\text{MgCl}_2$
 - Catalyst Synthesis: Particle Microreactor Example
 - Polyethylene and Isotactic PP: Donor Molecule Improvements
 - 4.3.2. Ethylene Propylene Copolymers (EPC)/Olefin Copolymers (OPC)
 - 4.3.3. Higher Olefins: Shell Higher Olefin Process (SHOP)

- 4.3.4. Styrene/ Butadiene Emulsion Polymerization
- 4.3.5. Polyethoxylates (Anionic)
- 4.3.6. Polyisobutylene (Cationic)
- 4.4. Future Catalysts: Late Transition Metals for Branched PE

Test – Chapters 3 & 4

5. Reduction Catalysis / Hydrogenation (Weeks 9 & 10)

5.1. Concepts

- 5.1.1. Reduction/Hydrogenation Catalyst Periodic Table
- 5.1.2. Thermodynamics
- 5.1.3. H₂ Activation by Metals
- 5.1.4. Hydroformylation: CO Insertion
- 5.1.5. Synthesis Gas Reactions
- 5.1.6. Non-Dissociative CO Adsorption: Methanol Synthesis Catalysts
- 5.1.7. CO Dissociation: Fischer-Tropsch
- 5.1.8. Schultz-Flory Distribution
- 5.1.9. Hydrodesulfurization

5.2. Elements of Catalyst Design

- 5.2.1. Metal Substitution: Fe vs. Co in Fischer-Tropsch
- 5.2.2. Metal / Ligand Effect: Hydroformylation
- 5.2.3. Hydroformylation Ligand Effect: Electronic and Steric
- 5.2.4. Asymmetric Hydrogenation
- 5.2.5. Promoters and Poisons

5.3. Major Industrial Processes

- 5.3.1. Hydrogenolysis: Hydrocracking/Hydrotreating
- 5.3.2. Aromatic Hydrogenation: Ethylbenzene to Styrene
- 5.3.3. Hydroformylation / Hydrogenation: Oxo Alcohols
- 5.3.4. Carbonylation: Methanol to Acetic Acid
- 5.3.5. Catalytic Reforming
- 5.3.6. Ammonia Synthesis - Haber-Bosch Process

6. Environmental Catalysis (Weeks 11 & 12)

6.1. Concepts

- 6.1.1. Exhaust Gas Periodic Table
- 6.1.2. Thermodynamic Considerations
- 6.1.3. Exhaust Gas Components C/soot/ash (PM), CH_x, NO_x, CO, SO_x, CO₂
- 6.1.4. Catalytic Conversion of Exhaust Gas Components
- 6.1.5. Catalysts for Removal of Exhaust Pollutants
- 6.1.6. 3- Way Catalyst Components
- 6.1.7. Lean NO_x Catalyst Components
- 6.1.8. SCR Catalyst Components
- 6.1.9. NO_x Absorber Catalyst Components
- 6.1.10. Diesel Oxidation Catalyst (DOC) and Diesel Particulate Trap (DPF) Catalyst Components
- 6.1.11. Mechanistic Concepts

- 6.2. Elements of Catalyst Design
 - 6.2.1. Metal substitutions
 - 6.2.2. Promoters & poisons
 - 6.2.3. Catalyst Synthesis
 - 6.2.4. Engineering Concepts
- 6.3. Major Catalytic Technologies
 - 6.3.1. Catalyzed Diesel particulate trap (CDPT) / soot oxidation
 - 6.3.2. Diesel Oxidation Catalyst (DOC)
 - 6.3.3. Selective catalytic reduction (SCR) NO_x reduction
 - 6.3.4. NO_x Trap
 - 6.3.5. 3-Way Catalyst – Gasoline Engines
- 6.4. Future Technology – Fuel Cells

Test – Chapters 5 & 6

7. Catalyst Characterization (Week 13)

- 7.1. Spectroscopic Methods
 - 7.1.1. X-ray Diffraction(XRD) /X-ray Fluorescence (XRF)
 - 7.1.2. X-ray Photoelectron Spectroscopy (XPS)
 - 7.1.3. Extended X-ray Adsorption Fine Structure (EXAFS)
 - 7.1.4. Fourier Transform Infrared (FTIR)
 - 7.1.5. Laser Raman Sprctroscopy
 - 7.1.6. Nuclear Magnetic Resonance Spectroscopy (NMR)
 - 7.1.7. Electron Microscopy (EM)
 - 7.1.8. Secondary Ion Mass Spectrometry (SIMS)
- 7.2. Adsorption Methods
 - 7.2.1. BET Surface Area
 - 7.2.2. Porosimetry – Pore Volume and Pore Size Distribution
 - 7.2.3. Thermogravimetric Analysis (TGA) / Differential Scanning Calorimetry (DSC)

Student Project Plan Presentations (Week 14)

Summary & Review (Week 15)

Final Exam (Week 16)