Contents

1 Introduction 1
1.1 Background 1
1.1.1 Purification of C2–C4 Olefins 1
1.1.2 Production of Ethylene from Acetylene 2
1.2 Properties of Selective Hydrogenation Reactions 3
1.3 Industrial Processes 3
1.4 Progress in Catalyst Development 6
1.4.1 Reaction Mechanism on Pd Catalyst 6
1.4.2 Influencing Factors on Pd-Based Catalysts 12
1.4.3 Pd-Based Bimetallic Catalysts 17
1.4.4 Non-Pd Catalysts 19
1.5 Thesis Outline 20
References 21

2 Experimental and Theoretical Methods 31
2.1 Chemicals and Instruments 31
2.2 Measurements of Model Surfaces 31
2.2.1 Ultra-High Vacuum (UHV) System 31
2.2.2 Preparation of Single-Crystal Surfaces 31
2.2.3 Temperature-Programmed Desorption (TPD) 33
2.3 Density Functional Theory (DFT) Calculations 34
2.4 Catalyst Preparation 34
2.4.1 Supported Catalyst 34
2.4.2 Mo_2C-Based Catalyst 35
2.5 Catalyst Characterization 35
2.5.1 SEM 35
2.5.2 TEM 36
2.5.3 XRD 36

2.5.4 TG-DTA . . . 36
2.5.5 Physisorption . . . 36
2.5.6 CO-Chemisorption . . . 36
2.5.7 XAFS . . . 37
2.6 Catalyst Evaluation . . . 38
2.6.1 Batch Reactor . . . 38
2.6.2 Fixed-Bed Reactor . . . 40
2.6.3 Slurry Reactor . . . 41
2.7 Measurement of Solubility . . . 41
References . . . 42

3 Selective Hydrogenation of 1,3-Butadiene on Pd–Ni Bimetallic Catalyst: From Model Surfaces to Supported Catalysts . . . 45
3.1 Introduction . . . 45
3.2 DFT Calculation . . . 47
3.2.1 Adsorption Energy . . . 47
3.2.2 Activation Barrier . . . 47
3.3 UHV Results . . . 49
3.3.1 Preparation of Single-Crystal Surfaces . . . 49
3.3.2 TPD Results . . . 52
3.4 Characterization of Supported Catalysts . . . 55
3.4.1 TEM . . . 56
3.4.2 CO Chemisorption . . . 56
3.4.3 XAFS . . . 56
3.5 Evaluation of Supported Catalysts . . . 60
3.5.1 Batch Reactor . . . 60
3.5.2 Fixed-Bed Reactor . . . 63
3.6 Discussion . . . 66
3.7 Conclusion . . . 68
References . . . 69

4 Effect of Oxide Supports on Pd–Ni Bimetallic Catalysts for 1,3-Butadiene Hydrogenation . . . 73
4.1 Introduction . . . 73
4.2 Catalyst Characterization . . . 74
4.2.1 TEM . . . 74
4.2.2 CO Chemisorption . . . 74
4.2.3 Temperature Programmed Reduction (TPR) . . . 76
4.2.4 XAFS . . . 77
4.3 Catalyst Evaluation . . . 79
4.3.1 Bimetallic Effect . . . 79
4.3.2 Hydrogenation Activity . . . 81
4.3.3 Selectivity . . . 82

4.4 Discussion . . . 84
4.4.1 Bimetallic Effect . . . 84
4.4.2 Support Effect . . . 84
4.5 Conclusion . . . 86
References . . . 87

5 Replacing Precious Metals with Carbide Catalysts for Hydrogenation Reactions . . . 89
5.1 Introduction . . . 89
5.2 Catalyst Characterization . . . 90
5.3 Mo_2C for the Hydrogenation of Dienes . . . 92
5.3.1 1,3-Butadiene . . . 93
5.3.2 1,3-Cyclohexadiene . . . 94
5.3.3 1,4-Cyclohexadiene . . . 95
5.4 Ni/Mo_2C for the Hydrogenation of 1,3-Butadiene . . . 97
5.5 Discussion . . . 98
5.5.1 Hydrogenation Activity and Stability . . . 98
5.5.2 Selectivity . . . 101
5.5.3 Potential Advantage in Cost Reduction . . . 103
5.6 Conclusion . . . 104
References . . . 104

6 Selective Hydrogenation of Acetylene in Liquid Phase: A Novel Process . . . 107
6.1 Introduction . . . 107
6.2 Catalyst Characterization . . . 109
6.3 Optimization of Operation Parameters . . . 110
6.3.1 Effect of Temperature . . . 111
6.3.2 Effect of GHSV . . . 113
6.3.3 Effect of H_2/C_2H_2 Ratio . . . 114
6.3.4 Comparison with Gas-Phase Reaction . . . 117
6.4 Solvent Effect . . . 118
6.4.1 Selective Solubility . . . 118
6.4.2 Viscosity . . . 119
6.5 Induction Period . . . 121
6.6 Catalyst Stability . . . 122
6.7 A Comparison with Solid Catalyst with Ionic Liquid Layer (SCILL) . . . 124
6.7.1 A General Comparison . . . 124
6.7.2 Selectivity . . . 126
6.7.3 Stability . . . 126
6.7.4 Discussion . . . 129

6.8 Process Optimization and Reactor Design 131
6.8.1 Two-Stage Slurry Reactor 132
6.8.2 Pressure Effect. 132
6.8.3 Design of Multi-Stage Reactor 134
6.9 Conclusion 135
References. 136

7 Conclusions 139

http://www.springer.com/978-981-10-0772-9

Catalytic and Process Study of the Selective Hydrogenation of Acetylene and 1,3-Butadiene

Hou, R.

2017, XII, 141 p. 83 illus., 42 illus. in color., Hardcover
ISBN: 978-981-10-0772-9