

Contents

Table of Contents	xiii
Notation	xvii
1 Introduction	1
1.1 Three-way catalysts	1
1.2 Oxygen storage materials	3
1.3 Thesis scope and outline	7
2 Lambda value, oxygen storage, and lumped concentrations	11
3 Measurements	21
3.1 Experimental setup and employed samples	21
3.2 Overview of measurements and setpoint calculation	24
3.3 Lambda sweep experiment (LS)	27
3.3.1 Fresh catalysts	27
3.3.2 Aged catalysts	33
3.4 Lambda sweep experiment with lambda cycling (LSC)	37
3.4.1 Fresh catalysts	37
3.4.2 Aged catalysts	48
3.5 Temperature sweep experiment with lambda-cycling (TSC)	54
3.5.1 Fresh catalysts	55
3.5.2 Aged catalysts	63
3.6 Lambda sensors	66
3.6.1 Switch-type sensor	66
3.6.2 Wideband sensor	67
3.7 Reproducibility	69
3.8 Summary	70
4 Mathematical Model	73
4.1 Three-way catalyst models	73
4.1.1 Detailed models	76
4.1.2 Simplified models	82
4.2 Model formulation	96

4.2.1	Model Solution	107
4.3	Summary	108
5	Parameter identification	111
5.1	Residual definition	111
5.2	Residual minimization	112
5.3	Parameter identifiability and subset selection	112
5.3.1	Sensitivity matrix calculation	115
6	Lambda sweep modeling	119
6.1	Fresh catalysts	126
6.1.1	Model analysis	126
6.1.2	Rich to lean (R2L) switches	129
6.1.3	Lean to rich (L2R) switches	134
6.1.4	Oxygen storage and release exceeding stoichiometric demand	137
6.1.5	Validation	139
6.1.6	Classification of different TWCs	141
6.2	Aged catalysts	144
6.2.1	Model analysis	144
6.2.2	Lambda switches	149
6.2.3	Validation and classification	153
6.3	Summary	156
7	Temperature sweep modeling	161
7.1	Fresh catalyst	162
7.1.1	Model analysis	162
7.1.2	Lambda switches	170
7.1.3	Classification	177
7.2	Aged catalysts	179
7.2.1	Model analysis	179
7.2.2	Lambda switches	181
7.2.3	Classification	188
7.3	Space velocity effects	189
7.4	Summary	192
8	Model extensions and application	197
8.1	Full model	199
8.1.1	Model equations	200
8.1.2	Lambda sweep modeling	202
8.2	Mixed model	209
8.2.1	Model equations	209
8.2.2	Lambda sweep modeling	211
8.3	Summary	218

9 Conclusions and outlook	221
A Optimization algorithms	225
B Selection of optimization algorithm	231
B.1 Lumped model	231
B.2 Full model	233
C Further model details	235
D Mass spectrometer setup	243
Bibliography	245