

# Content

Zusammenfassung .....	ii
Abstract .....	iv
Content .....	v
Abbreviations .....	ix
Introduction and experimental background.....	1
Introduction .....	2
Energy storage.....	2
Methanol steam reforming .....	2
Outline of this work.....	4
Experimental background.....	5
Mass spectrometry (MS) .....	5
Gas chromatography (GC) .....	5
X-rays sources.....	5
X-ray diffraction (XRD).....	6
X-ray fluorescence spectroscopy .....	6
X-ray absorption spectroscopy (XAS) .....	6
X-ray absorption near edge spectroscopy (XANES).....	7
Extended X-ray absorption fine spectroscopy (EXAFS) .....	9
Diffuse reflectance ultraviolet and visual spectroscopy (DR-UV/Vis) .....	9
Determination of surface areas.....	10
N <sub>2</sub> physisorption .....	10
Temperature-programmed reduction (TPR).....	10
Determination of Cu surface areas .....	11
Chapter I Influence of calcination on structural configuration of CuO <sub>x</sub> particles in CuO <sub>x</sub> /SBA-15 catalysts .....	13
I.1 Introduction.....	14
I.2 Experimental .....	16
I.2.1 Synthesis.....	16
I.2.2 N <sub>2</sub> physisorption.....	17
I.2.3 X-ray fluorescence analysis (XRF).....	17
I.2.4 X-ray diffraction (XRD).....	17
I.2.5 Diffuse reflectance ultraviolet/visible-light spectroscopy (DR-UV/Vis) .....	18
I.2.6 X-ray absorption spectroscopy (XAS) .....	18

I.3	Results and discussion .....	19
I.3.1	Composition of oxidic precursors.....	19
I.3.2	Preliminary study on support stability using N <sub>2</sub> physisorption .....	19
I.3.3	Mesoporous structure of oxidic precursors.....	21
I.3.4	Cu atom density on silica surface.....	23
I.3.5	X-ray diffraction of oxidic precursors .....	24
I.3.6	DR-UV/Vis of oxidic precursors .....	25
I.3.7	Estimation of CuO <sub>x</sub> particle sizes from optical band gap .....	28
I.3.8	X-ray absorption near edge spectroscopy (XANES).....	30
I.3.9	Extended X-ray absorption fine structure (EXAFS).....	32
I.3.10	Refinement of EXAFS spectra of thin layer precursors.....	33
I.3.11	Refinement of EXAFS spectra of thick layer precursors .....	36
I.3.12	Processes during calcination.....	37
I.3.13	Constitution of CuO <sub>x</sub> particles.....	38
I.3.14	Electronic structure of CuO <sub>x</sub> particles .....	40
I.3.15	Proposed structure of CuO <sub>x</sub> /SBA-15 precursors .....	41
I.3.16	Comparison to other supported metal oxide particles .....	43
I.4	Conclusions .....	43
 Chapter II	Formation, structural and catalytic characterization of methanol steam reforming Cu/SBA-15 catalysts .....	45
II.1	Introduction .....	46
II.2	Experimental .....	48
II.2.1	Temperature-programmed reduction and determination of Cu surface area .....	48
II.2.2	Methanol steam reforming (MSR) .....	49
II.2.3	In situ X-ray diffraction (XRD) .....	51
II.2.4	In situ X-ray absorption spectroscopy (XAS).....	52
II.3	Results and discussion .....	52
II.3.1	Activation of oxidic precursors during TPR up to 250 °C .....	52
II.3.2	XAS at Cu K edge of oxidic precursors during TPR and application of linear combination of reference XANES spectra .....	54
II.3.3	Oxidation state of Cu metal particles supported on SBA-15 during TPR and MSR.....	57
II.3.4	Effect of Cu particle size on Cu K edge XANES profile .....	59
II.3.5	EXAFS of Cu/SBA-15 catalysts at Cu K edge after TPR during MSR .....	60
II.3.6	XRD of Cu/SBA-15 catalysts during activation and MSR.....	63
II.3.7	Cu surface areas of Cu/SBA-15 catalysts .....	66
II.3.8	Methanol steam reforming over Cu/SBA-15 catalysts .....	68

II.3.9	Size of Cu metal particles supported on SBA-15 .....	71
II.3.10	Microstrain of Cu metal particles supported on SBA-15 .....	73
II.3.11	Evaluation of microstrain obtained from XRD and static disorder obtained from XAS ..	75
II.3.12	Structure activity correlations of thin layer catalysts .....	75
II.3.13	Structure activity correlations of thick layer catalysts.....	78
II.3.14	Relationships between Cu particle size and disorder in Cu particles and catalytic activity in methanol steam reforming .....	81
II.3.15	Mechanism of methanol steam reforming .....	84
II.3.16	Deactivation of Cu/SBA-15 catalysts during methanol steam reforming .....	85
II.4	Conclusions .....	87
<b>Chapter III</b>	<b>Impact of redox pretreatment on structure and activity of Cu/SBA-15 catalysts in methanol steam reforming .....</b>	<b>89</b>
III.1	Introduction.....	90
III.2	Experimental .....	91
III.2.1	In situ X-ray diffraction (XRD) during methanol steam reforming and temporary oxygen co-feeding .....	91
III.2.2	In situ X-ray absorption (XAS) during methanol steam reforming and temporary O <sub>2</sub> addition.....	91
III.2.3	Redox activation of Cu/SBA-15 catalysts and Cu surface areas and activity in methanol steam reforming.....	92
III.2.4	In situ X-ray absorption spectroscopy (XAS) at the Cu K edge during redox activation..	92
III.3	Results and discussion .....	93
III.3.1	Increased activity after temporary O <sub>2</sub> addition to methanol steam reforming feed .....	93
III.3.2	Evolution of Cu metal particles during temporary O <sub>2</sub> addition observed by in situ XAS	94
III.3.3	Impact of oxygen co-feeding on Cu metal particles observed by in situ XRD .....	97
III.3.4	Effect of oxygen co-feeding on Cu/SBA-15 catalysts.....	99
III.3.5	Temperature-programmed reduction (TPR) during redox activation .....	99
III.3.6	Phase transformation during first and second reduction of redox activation using LC- XANES fit .....	101
III.3.7	XANES of oxidic precursors and intermediate stage CuO <sub>x</sub> /SBA-15 .....	102
III.3.8	EXAFS at Cu K edge of oxidic precursors and intermediate CuO <sub>x</sub> /SBA-15 .....	104
III.3.9	Correlation between static disorder in CuO <sub>x</sub> particles and reducibility.....	106
III.3.10	EXAFS of Cu/SBA-15 catalysts after standard activation and after redox activation....	107
III.3.11	Impact of redox activation on Cu surface areas.....	110
III.3.12	Methanol steam reforming after redox activation.....	111
III.3.13	Evolution of Cu metal particles during redox activation.....	114

III.3.14 Activity in methanol steam reforming after redox treatment .....	116
III.4 Conclusions .....	117
General conclusions and outlook .....	119
CuO <sub>x</sub> /SBA-15 model system as oxidic precursor.....	120
Cu/SBA-15 model catalysts in methanol steam reforming.....	120
Microstrain in Cu metal particles.....	122
Appendix .....	xi
DR-UV/Vis.....	xii
XAS refinements of oxidic precursors.....	xiv
Temperature-programmed reduction (TPR) .....	xvi
Sideproducts in methanol steam reforming .....	xvii
XAS during oxygen co-feeding .....	xviii
Bibliography .....	xxi
Epilogue.....	xxxi
Danksagung.....	xxxii