

Content

<i>Zusammenfassung</i>	<i>ii</i>
<i>Abstract</i>	<i>iv</i>
<i>Content</i>	<i>v</i>
<i>Abbreviations</i>	<i>ix</i>
Introduction and experimental background	1
<i>Introduction</i>	2
Energy storage	2
Methanol steam reforming.....	2
<i>Outline of this work</i>	4
<i>Experimental background</i>	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 ₂ physisorption.....	10
Temperature-programmed reduction (TPR)	10
Determination of Cu surface areas	11
Chapter I Influence of calcination on structural configuration of CuO_x particles in CuO_x/SBA-15 catalysts	13
<i>I.1 Introduction</i>	14
<i>I.2 Experimental</i>	16
I.2.1 Synthesis	16
I.2.2 N ₂ 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>I.3 Results and discussion</i>	19
I.3.1 Composition of oxidic precursors	19
I.3.2 Preliminary study on support stability using N ₂ 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 _x 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 _x particles.....	38
I.3.14 Electronic structure of CuO _x particles	40
I.3.15 Proposed structure of CuO _x /SBA-15 precursors	41
I.3.16 Comparison to other supported metal oxide particles.....	43
<i>I.4 Conclusions</i>	43

Chapter II Formation, structural and catalytic characterization of methanol steam reforming Cu/SBA-15 catalysts **45**

<i>II.1 Introduction</i>	46
<i>II.2 Experimental</i>	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
<i>II.3 Results and discussion</i>	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	<i>Conclusions</i>	87
Chapter III Impact of redox pretreatment on structure and activity of Cu/SBA-15 catalysts in methanol steam reforming		89
III.1	<i>Introduction</i>	90
III.2	<i>Experimental</i>	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 ₂ 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	<i>Results and discussion</i>	93
III.3.1	Increased activity after temporary O ₂ addition to methanol steam reforming feed	93
III.3.2	Evolution of Cu metal particles during temporary O ₂ 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 _x /SBA-15	102
III.3.8	EXAFS at Cu K edge of oxidic precursors and intermediate CuO _x /SBA-15	104
III.3.9	Correlation between static disorder in CuO _x 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
<i>CuO_x/SBA-15 model system as oxidic precursor</i>	120
<i>Cu/SBA-15 model catalysts in methanol steam reforming</i>	120
<i>Microstrain in Cu metal particles</i>	122
Appendix	xi
<i>DR-UV/Vis</i>	xii
<i>XAS refinements of oxidic precursors</i>	xiv
<i>Temperature-programmed reduction (TPR)</i>	xvi
<i>Sideproducts in methanol steam reforming</i>	xvii
<i>XAS during oxygen co-feeding</i>	xviii
Bibliography	xxi
Epilogue	xxx
<i>Danksagung</i>	xxxii