

TABLE OF CONTENTS

A	INTRODUCTION AND MOTIVATION	1
A.1	Homogeneous and heterogeneous metal catalysis	2
A.1.1	Conventional preparation techniques for active metal sites on oxidic supports ^[6] ...	4
A.1.2	Grafting and surface organometallic chemistry (SOMC)	8
A.2	Molecular mechanisms in metal catalysis	10
A.2.1	Oxidative dehydrogenation	12
A.2.2	HECK coupling reaction	14
A.2.2.1	The leaching phenomenon	15
A.3	Spectroscopic methods in molecular surface chemistry.....	17
A.3.1	IR-spectroscopy ^[33]	17
A.3.2	Electron paramagnetic resonance spectroscopy (EPR).....	20
A.4	Motivation.....	26
B	RESULTS AND DISCUSSION.....	29
B.1	The support Aerosil® 200.....	30
B.2	Single-site vanadium surface complexes.....	32
B.2.1	Grafting of monomeric vanadium precursors	39
B.2.1.1	Vanadyl(V) tris-(isopropoxide) grafted on SiO ₂ ⁷⁰⁰	40
B.2.1.1.1	<i>In situ</i> EPR monitoring of the reaction of oxygen and propane with VO(O ⁱ Pr) ₃ /SiO ₂ ⁷⁰⁰	45
B.2.1.1.2	Adsorption of oxygen on VO(O ⁱ Pr) ₃ /SiO ₂ ⁷⁰⁰	48
B.2.1.1.3	<i>In situ</i> oxidation and reduction of VO(O ⁱ Pr) ₃ /SiO ₂ ⁷⁰⁰	50
B.2.1.1.4	Summarizing discussion of VO(O ⁱ Pr) ₃ grafted on SiO ₂ ⁷⁰⁰	54
B.2.1.2	Vanadyl(IV) bisacetylacetonate grafted on SiO ₂ ⁷⁰⁰	55
B.2.1.2.1	Quantification of grafted vanadium species by UV/Vis and EPR spectroscopy	56
B.2.1.2.2	Spectroscopic characterization by EPR	60
B.2.1.2.3	<i>In situ</i> grafting of vanadyl(IV) bisacetylacetonate monitored by EPR	65
B.2.1.2.4	Reactivity towards Hydrogen and Oxygen (TPR and TPO).....	67
B.2.1.2.5	Summarizing discussion of VO(acac) ₂ grafted on SiO ₂ ⁷⁰⁰	76
B.2.2	Grafting of dimeric bis-(μ-oxo)-bisvanadyl(V) bisacetylacetonate.....	78
B.2.2.1	The precursor (VO) ₂ (μ-O) ₂ (acac) ₂	78
B.2.2.2	(VO) ₂ (μ-O) ₂ (acac) ₂ Grafted on SiO ₂ ⁷⁰⁰	80
B.2.2.3	Reactivity towards oxygen and low hydrocarbons	84
B.2.2.4	Combined XANES- and EXAFS study.....	86
B.2.2.5	Summarizing discussion of (VO) ₂ (μ-O) ₂ (acac) ₂ grafted on SiO ₂ ⁷⁰⁰	88

B.2.3	Single-site vanadyl-oxygen surface complex	89
B.2.4	Single-site oxo-vanadium complexes on surfaces: summarizing evaluation and prospects for ODH.....	97
B.3	Single-site palladium surface complexes	100
B.3.1	Challenges in working with alkyl palladium complexes	101
B.3.2	Grafting of dimethylpalladium(II) complexes on SiO ₂	102
B.3.3	Characterization of palladium surface complexes	104
B.3.3.1	IR spectroscopy	105
B.3.3.1.1	Thermal decomposition of PdMe ₂ (tmeda) grafted on SiO ₂ ⁷⁰⁰	107
B.3.3.1.2	Thermal decomposition of PdMe ₂ (dppe) grafted on SiO ₂ ⁷⁰⁰	110
B.3.3.1.3	<i>in situ</i> IR spectroscopy of CO adsorption	111
B.3.3.1.4	CO-adsorption on PdMe ₂ (tmeda) grafted on SiO ₂ ⁷⁰⁰	113
B.3.3.1.5	CO-adsorption on freshly grafted PdMe ₂ (dppe)/SiO ₂ ⁷⁰⁰	119
B.3.3.1.6	Summarizing discussion of the IR spectroscopic characterization	121
B.3.3.2	Temperature programmed reactions	123
B.3.3.2.1	Temperature programmed reactions with PdMe ₂ (tmeda) on SiO ₂ ⁷⁰⁰	127
B.3.3.2.2	Temperature programmed reactions with PdMe ₂ (dppe) grafted on SiO ₂ ⁷⁰⁰	141
B.3.3.2.3	Summarizing discussion of temperature programmed reactions.....	148
B.3.3.3	Transmission electron microscopic investigation	150
B.3.3.4	¹ H, ¹³ C and ³¹ P MAS NMR spectroscopy	155
B.3.4	Summarizing discussion on challenges in characterization of isolated palladium surface complexes.....	158
B.3.5	Investigation of the catalytic activity of molecular palladium surface complexes in HECK reactions	161
B.3.5.1	HECK coupling with chlorobenzene as a demanding model reaction	166
B.3.5.2	Role of the additive	167
B.3.5.3	Variation of the precursor	169
B.3.5.4	Variation of the metal loading	171
B.3.5.5	Oxidative and reductive pre-treatment of the catalysts	174
B.3.5.6	Comparison with literature results.....	176
B.3.5.7	Side reactions and dehalogenation.....	177
B.3.6	Summarizing discussion of the catalytic performance of palladium surface complex in HECK reactions.....	179
C	SUMMARY.....	181
D	ZUSAMMENFASSUNG.....	185
E	EXPERIMENTAL.....	189
E.1	General working techniques	190

E.2	Syntheses of isolated surface metal complexes	190
E.2.1	Pre-treatment of the support	192
E.2.2	Synthesis surface-bound vanadium complexes	192
E.2.2.1	Grafting of tris(isopropoxide) vanadyl(V) on SiO ₂ ⁷⁰⁰	192
E.2.2.2	Grafting of bis-(μ-oxo)-bisvanadyl(V) bisacetylacetonate on SiO ₂ ⁷⁰⁰	193
E.2.2.3	Grafting of vanadyl(IV) bis-(acetylacetonate) on SiO ₂ ⁷⁰⁰	193
E.2.3	Synthesis of surface-bound palladium(II) complexes	194
E.2.3.1	Synthesis of dimethyl-(N,N,N,N-tetramethylethylenediamine) palladium(II)	194
E.2.3.2	Synthesis of dimethyl-(2,2'-bipyridyl) palladium(II) and dimethyl-(1,2-bis-(diphenylphosphino)-ethane) palladium(II)	194
E.2.3.3	Grafting of dimethyl-(ligand) palladium(II) complexes on SiO ₂ ⁷⁰⁰	195
E.3	Atmospheric post-treatment and catalytic application	196
E.3.1	Reduction and oxidation of the materials	196
E.3.2	HECK reaction	197
E.4	Analytical techniques and characterization	198
E.4.1	Spectroscopic analysis	198
E.4.1.1	Nuclear magnetic resonance spectroscopy (NMR)	198
E.4.1.2	Magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR)	198
E.4.1.3	Electron paramagnetic resonance spectroscopy (EPR)	198
E.4.1.4	Infrared spectroscopy (IR)	201
E.4.1.5	Ultra violet and visible light spectroscopy (UV/Vis)	204
E.4.2	Gas chromatographic analysis	205
E.4.3	Transmission electron microscopy	206
E.4.4	Gas supply systems and atmospheric treatments	206
E.4.4.1	Temperature programmed reduction and oxidation	206
E.4.5	Elemental analyses	208
F	REFERENCES	209
G	APPENDIX	219
G.1	Supplemental graphs and figures	220
G.2	Conference contributions	232
G.3	Publications	232