

Contents

1. Introduction	1
1.1. Selective Oxidation of Alkanes	2
1.2. Traditional Concepts in Heterogeneous Selective Oxidation	3
1.3. Alkane Oxidation over Semiconducting Bulk Oxides	6
1.4. The Investigation of Charge Transport and Charge Transfer	9
1.5. Aims and Outline of the Present Thesis	10
2. The Microwave Cavity Perturbation Technique	13
2.1. Cavity Resonators and Cavity Modes	13
2.2. The Theory behind the MCPT	15
2.3. Experimental Considerations of the <i>Operando</i> MCPT Setup	18
2.4. Reflection Coefficient and <i>Q</i> Factor Determination	19
3. The Electronic Structure of V_2O_{5-x} in Alkane Oxidation Gas Feeds	23
3.1. Abstract	23
3.2. Introduction	23
3.3. Experimental Section	25
3.4. Results	26
3.4.1. Redox Response of V_2O_{5-x} in Alkane Oxidation Feeds	26
3.4.2. Resonant Photoelectron Spectroscopy (resPES)	30
3.5. Discussion	34
3.5.1. Gas-Phase-Induced Response of V_2O_{5-x} Electronic Structure	34
3.5.2. ResPES: V_2O_{5-x} Valence Band Spectra	35
3.6. Conclusions	37
4. <i>Operando</i> MCPT Study on Vanadia Oxidation Catalysts	39
4.1. Abstract	39
4.2. Introduction	39
4.3. Experimental Section	41
4.3.1. Catalysts	41
4.3.2. Microwave Cavity Perturbation Technique and Catalytic Testing	41
4.3.3. Diffuse Reflectance UV-Vis Spectroscopy	43
4.4. Results	43
4.4.1. Catalytic Behavior	43
4.4.2. Correlations between Permittivity/Conductivity and Catalytic Performance	43
4.4.3. Response of Conductivity to Reversible Redox Reaction	45
4.4.4. Temperature Dependence of Conductivity and Permittivity	49
4.5. Discussion	52
4.5.1. General Remarks to Conductivity and Selective Oxidation	52
4.5.2. Relation between Catalytic Performance and Conductivity	53
4.6. Conclusions	56
5. Electronic and Dielectric Properties of MoV-Oxide	59
5.1. Abstract	59
5.2. Introduction	59

5.3. Experimental Section	60
5.3.1. Catalyst	60
5.3.2. Microwave Cavity Perturbation Technique (MCPT)	61
5.3.3. NAP-XPS and NEXAFS	61
5.4. Results	62
5.4.1. MCPT Permittivity and Conductivity	62
5.4.2. NAP-XPS and NEXAFS	67
5.5. Discussion	73
5.5.1. On the Origin of the Conductivity or Permittivity Response	73
5.5.2. Comparison of MoV-Based Oxide Catalysts	75
5.5.3. The Influence of Steam	77
5.6. Conclusions	79
6. Overview of Vanadia Oxidation Catalysts	81
7. Thesis Summary and Final Conclusion	85
Appendices	89
A. SI The Electronic Structure of V_2O_{5-x} in Alkane Oxidation Gas Feeds	91
B. SI <i>Operando</i> MCPT Study on Vanadia Oxidation Catalysts	103
C. SI Electronic and Dielectric Properties of MoV-Oxide	121
Bibliography	141