
PREFACE.....	6
1 INTRODUCTION.....	9
1.1 From oil to renewables.....	9
1.2 Green and sustainable chemistry.....	11
1.3 Biorefineries.....	12
1.4 Cellulosic biomass to fuels.....	13
1.4.1 Biomass gasification.....	13
1.4.2 Biomass hydrolysis.....	14
1.4.3 Bio-oil.....	14
1.4.3.1 Bio-oil from fast pyrolysis.....	15
1.4.3.2 Bio-oil from liquefaction.....	15
1.5 Vegetable oils and animal fats to fuels.....	16
1.6 Platform chemicals for biorefineries.....	17
1.7 Glycerochemistry.....	19
1.7.1 Production of acrolein and acrylic acid from glycerol.....	20
1.7.2 Life Cycle Assessment (LCA) for the production of acrolein from glycerol.....	23
1.8 Vanadium substituted HTBs: complex mixed-oxides for glycerol oxidehydration to acrylic acid.....	24
2 EXPERIMENTAL.....	33
2.1 Catalyst synthesis.....	33
2.1.1 Hydrothermal synthesis of HTBs.....	33
2.1.2 Ion-exchange and Incipient wetness impregnation.....	34
2.1.3 Hydrothermal synthesis of modified AlPO-5.....	36
2.1.4 Slurry synthesis of a M_5O_{14} -like oxide.....	37
2.2 Catalyst characterization.....	37
2.2.1 Surface area and textural properties.....	37
2.2.2 Scanning electron microscopy (SEM).....	39
2.2.3 Transmission electron microscopy (TEM).....	40
2.2.4 Powder X-ray Diffraction (Powder-XRD).....	41
2.2.5 Fourier transform infrared spectroscopy (FTIR).....	42
2.2.6 X-ray absorption spectroscopy (XAS).....	43
2.2.7 Pulse chemisorption and temperature-programmed desorption of ammonia.....	44
2.2.8 FTIR of adsorbed carbon monoxide or ammonia.....	45
2.2.9 Raman spectroscopy.....	46
2.2.10 X-ray photoelectron spectroscopy (XPS).....	47

2.3	Catalytic testing	49
3	RESULTS AND DISCUSSION.....	53
3.1	Introduction of Niobium in V-substituted HTBs.....	53
	3.1.1 <i>Physicochemical properties of the oxides</i>	53
	3.1.2 <i>Lab-scale reactor tests</i>	58
	3.1.3 <i>Conclusions</i>	65
3.2	Nb- and V-substituted HTBs: the influence of reaction conditions on catalytic performance in glycerol oxidehydration.....	67
	3.2.1 <i>Physicochemical properties of the oxides</i>	67
	3.2.2 <i>Lab-scale reactor tests</i>	73
	3.2.3 <i>Conclusions</i>	84
	3.2.4 <i>Notes on reaction conditions and process safety</i>	85
3.3	Introduction of Molybdenum in V-substituted HTBs.....	87
	3.3.1 <i>Physicochemical properties of the oxides</i>	87
	3.3.2 <i>Lab-scale reactor tests</i>	93
	3.3.3 <i>Conclusions</i>	105
3.4	The importance of acid-redox properties and structure-reactivity correlations in one-pot glycerol oxidehydration.....	106
	3.4.1 <i>Physicochemical properties of the oxides</i>	107
	3.4.2 <i>Lab-scale reactor tests</i>	113
	3.4.3 <i>Conclusions</i>	125
3.5	X-ray Absorption Spectroscopy (XAS) with synchrotron radiation as a tool to better comprehend the complex structure of substituted-HTBs... ..	127
	3.5.1 <i>From reagents to HTBs</i>	128
	3.5.2 <i>Vanadium coordination in HTBs</i>	131
4	OVERALL CONCLUSIONS.....	134
5	PUBLICATIONS.....	136
5.1	Publications related to the research project presented in this PhD thesis.....	136
5.2	Publications related to other projects.....	136
6	BIBLIOGRAPHY.....	137
	APPENDIX.....	144
	(i) Summary in English.....	144
	(ii) Summary in Spanish.....	145
	(iii) Summary in Valencian.....	146
	Acknowledgements.....	147
