Contents

Chapter 1		**Introduction**	**1**
1.1		Overview	1
1.2		Structures of Polyoxometalates	2
	1.2.1	The Keggin structure	2
	1.2.2	The Well-Dawson structure	4
	1.2.3	The Anderson-Evans structure	5
	1.2.4	The Dexter-Silverton structure	5
	1.2.5	Transition Metal substituted Sandwich type Polyoxometalates	6
	1.2.6	Zinc and Cobalt based Sandwich type Polyoxometalates	8
1.3		Historical Background	9
1.4		Nomenclature in Heteropolyoxometalates	10
1.5		Crystal Structure of Keggin type Polyoxometalates	11
	1.5.1	Primary structure	11
	1.5.2	Secondary structure	11
	1.5.3	Tertiary structure	12
1.6		General Properties of Heteropoly Compounds	13
	1.6.1	Solubility of heteropoly compounds	13
	1.6.2	Redox properties of heteropoly compounds	14
	1.6.3	Acidic properties of heteropoly compounds	15
	1.6.4	Thermal properties of heteropoly compounds	16
1.7		Catalytic Applications of Polyoxometalates	17
	1.7.1	Polyoxometalates as catalysts in Industrial processes	17
	1.7.2	Catalytic applications of the Keggin type Polyoxometalates in Oxidation reactions	18
	1.7.3	Catalytic applications of the Sandwich type Polyoxometalates in Oxidation reactions	19
	1.7.4	Catalytic applications of the Anderson type Polyoxometalates in Oxidation reactions	20
1.8		Heterogenization of Polyoxometalates	20
1.9		Scope and Organization of the Thesis	22
	1.9.1	Scope and Objective of the present work	22

	1.9.2	Organization of the Thesis	23
Chapter 2		**Selective oxidation of alkenes and alcohols over $[SbW_9O_{33}]$ based catalyst system with *aq.* H_2O_2**	**30**
2.1		Introduction	30
2.2		Experimental	31
	2.2.1	Materials	31
	2.2.2	Catalyst synthesis	32
	2.2.2.1	Synthesis of $Na_9[SbW_9O_{33}].19.5H_2O$	32
	2.2.2.2	Synthesis of $Na_{11}(NH_4)\{[Mn(H_2O)]_3(SbW_9O_{33})_2\}.45H_2O$	32
	2.2.2.3	Synthesis of $K_{12}\{[Zn(H_2O)]_3(SbW_9O_{33})_2\}.46H_2O$	32
	2.2.3	Characterization of the catalysts	32
	2.2.4	Catalytic Reactions	33
	2.2.4.1	Preparation of catalyst stock solutions	33
	2.2.4.2	Procedure for the epoxidation of alkenes	33
	2.2.4.3	Procedure for the oxidation of alcohols	34
2.3		Results and Discussions	34
	2.3.1	Characterization of the catalysts	34
	2.3.2	Catalytic studies	37
	2.3.2.1	Catalytic activity of $Na_{11}(NH_4)\{[Mn(H_2O)]_3(SbW_9O_{33})_2\}$	37
	2.3.2.2	Effect of solvents on limonene epoxidation	40
	2.3.2.3	Effect of temperature on limonene epoxidation	41
	2.3.2.4	Epoxidation of other alkenes	43
	2.3.2.5	Oxidation of secondary and allylic alcohols	46
	2.3.2.6	Effect of temperature on cyclohexanol oxidation	49
	2.3.2.7	Effect of substrate: oxidant ratio on cyclohexanol oxidation	51
	2.3.3	Active Center of the Catalyst and reaction mechanism	53
2.4		Summary and Conclusions	56
Chapter 3		**Alkenes epoxidation catalyzed by vanadium heteropoly acids heterogenized on amine functionalized SBA-15 materials**	**59**
3.1		Introduction	59

3.2		Experimental	60
	3.2.1	Materials	60
	3.2.2	Synthesis of SBA-15	61
	3.2.3	Preparation of amine-functionalized SBA-15	61
	3.2.4	Preparation of vanadomolybdophosphoric acids	61
	3.2.4.1	Monovanadomolybdophosphoric acid, $H_4PMo_{11}VO_{40}$	62
	3.2.4.2	Divanadomolybdophosphoric acid, $H_5PMo_{10}V_2O_{40}$	62
	3.2.4.3	Trivanadomolybdophosphoric acid, $H_6PMo_9V_3O_{40}$	63
	3.2.5	Anchoring of vanadomolybdophosphoric acids onto NH_2-SBA	63
	3.2.6	Characterization	63
	3.2.7	Catalytic activity	64
3.3		Results and Discussions	65
	3.3.1	Synthesis and Characterization	65
	3.3.2	Spectroscopic studies	69
	3.3.3	Catalytic activity and catalyst recycling	72
	3.3.4	Reaction mechanism for neat V_xHPA	79
	3.3.4.1	UV-visible spectroscopy	79
	3.3.4.2	^{51}V NMR spectroscopy	81
	3.3.4.3	EPR spectroscopy	81
	3.3.4.4	Mechanism	83
3.4		Summary and Conclusions	85
Chapter 4		**Alkene epoxidation catalyzed by vanadium heteropoly acids dispersed on hydrated titania**	**89**
4.1		Introduction	89
4.2		Experimental	90
	4.2.1	Materials	90
	4.2.2	Preparation of vanadomolybdophosphoric acids	90
	4.2.2.1	Monovanadomolybdophosphoric acid, $H_4PMo_{11}VO_{40}$	91
	4.2.2.2	Divanadomolybdophosphoric acid, $H_5PMo_{10}V_2O_{40}$	91
	4.2.2.3	Trivanadomolybdophosphoric acid, $H_6PMo_9V_3O_{40}$	91
	4.2.3	Sample Preparation	92

	4.2.4	Characterization	92
	4.2.5	Catalytic activity	93
4.3		Results and Discussion	93
	4.3.1	Catalyst characterization	93
	4.3.2	Effect of solvent on the reaction	96
	4.3.3	Epoxidation of cyclooctene with different 15 wt% HPA/MO_2	97
	4.3.4	Effect of temperature and substrate: oxidant ratio on cyclooctene epoxidation	99
	4.3.5	Epoxidation of other alkenes	101
4.4		Summary and Conclusion	103
Chapter 5		**Selective oxidation of ethane to acetic acid over $MoVAlO_x$ based catalytic system with molecular oxygen**	**106**
5.1		Introduction	106
5.2		Experimental	107
	5.2.1	Catalyst preparation and Characterization	107
	5.2.2	Catalytic activity testing	108
5.3		Results	110
	5.3.1	Synthesis and Characterization	110
	5.3.1.1	Synthesis, elemental composition and surface properties	110
	5.3.1.2	Powder X-Ray diffraction	111
	5.3.1.3	Morphology of $MoAlVO_x$ catalysts	112
	5.3.1.4	Raman Spectroscopy	113
	5.3.1.5	UV-visible spectroscopy	115
	5.3.1.6	EPR Spectroscopy	118
	5.3.2	Selective Oxidation of ethane	120
5.4		Discussion	127
5.5		Summary and Conclusion	131
Chapter 6		**Summary and Conclusion**	**134**