

# Contents

<b>Summary</b>	<b>7</b>
<b>1. General introduction</b>	
1.1. Nature of amorphous aluminosilicates (ASAs) and their use	15
1.2. Synthesis routes	16
1.3. The acidity of ASAs	17
1.3.1. Characterization of acidity	17
1.3.2. Nature of the acid sites	18
1.4. Aim of the thesis	22
<b>2. Synthesis of amorphous aluminosilicates by grafting</b>	
2.1. Preparation of ASAs by grafting	23
2.1.1. Chemical Liquid Deposition	23
2.1.2. Chemical Vapour Deposition	24
2.2. Impact of grafting on the final properties of ASAs	26
2.2.1. Al/SiO <sub>2</sub>	26
2.2.2. Si/Al <sub>2</sub> O <sub>3</sub>	27
<b>3. Experimental</b>	
3.1. Description of the experimental set-ups	29
3.1.1. Chemical Liquid Deposition	29
3.1.2. Chemical Vapour Deposition	29
3.2. Synthesis of the materials	30
3.2.1. Si/Al <sub>2</sub> O <sub>3</sub>	30
3.2.2. Al/SiO <sub>2</sub>	31
3.2.3. List of samples	32
3.3. Characterization	33
3.3.1. Texture	33
3.3.2. Composition	33
3.3.3. Hydroxyl density	33
3.3.4. CO adsorption followed by infrared spectroscopy (IR)	33
3.3.5. <i>m</i> -xylene isomerization	34
3.3.6. Ethanol adsorption and desorption followed by thermogravimetry (TGA)	34

<b>4. Synthesis of amorphous aluminosilicates by grafting: tuning the building and final structure of the deposit by selecting the appropriate synthesis conditions</b>	
4.1. Introduction	37
4.2. Experimental	39
4.2.1. Nuclear magnetic resonance (NMR)	39
4.2.2. Transmission electron microscopy (TEM)	39
4.2.3. Time-of-flight secondary ion mass spectrometry (ToF-SIMS)	39
4.3. Results	39
4.3.1. Surface reactivity	39
4.3.2. Texture	41
4.3.3. Structure of the deposit	44
4.4. Discussion	55
4.4.1. Key parameters of grafting	55
4.4.2. Impact of the experimental conditions of grafting	58
4.5. Conclusion	60
<b>5. Quantification of Brønsted acid sites of grafted amorphous silica-aluminas and their turnover frequency in <i>m</i>-xylene isomerization</b>	
5.1. Introduction	61
5.2. Results	62
5.2.1. Preferential adsorption of ethanol on alumina surfaces	62
5.2.2. Dehydration of ethanol	66
5.2.3. <i>m</i> -xylene isomerization	68
5.2.4. CO adsorption followed by infrared spectroscopy	69
5.3. Discussion	76
5.3.1. Surface occupancy and distribution of silicon species on $\gamma$ -alumina	76
5.3.2. Active sites for ethanol dehydration and <i>m</i> -xylene isomerization	76
5.3.3. Non-selective grafting of silicon atoms on the facets of $\gamma$ -alumina by CVD-400°C	83
5.4. Conclusion	83
<b>6. Creation of Brønsted acidity by grafting aluminium isopropoxide on silica in controlled conditions: determination of the number of Brønsted sites and their turnover frequency in <i>m</i>-xylene isomerization</b>	
6.1. Introduction	85
6.2. Experimental: Adsorption of 2,6-lutidine followed by infrared spectroscopy	86
6.3. Results	86
6.3.1. Adsorption of ethanol followed by thermogravimetry	86
6.3.2. CO adsorption followed by infrared spectroscopy	90
6.3.3. <i>m</i> -xylene isomerization	95
6.4. Discussion	96
6.4.1. Surface occupancy and distribution of aluminium species on silica	96
6.4.2. Brønsted acid sites as active sites for ethanol dehydration and <i>m</i> -xylene isomerization	96
6.4.3. Comparison with Si/Al <sub>2</sub> O <sub>3</sub> grafting and zeolite	101

6.5. Conclusion	101
<b>7. The variety of Brønsted acid sites in amorphous aluminosilicates and zeolites</b>	
7.1. Introduction	103
7.2. Results	104
7.2.1. Ethanol adsorption and dehydration followed by thermogravimetry	104
7.2.2. Infrared spectroscopy	106
7.2.3. Isomerization of <i>m</i> -xylene	115
7.3. Discussion	115
7.3.1. Zeolitic Brønsted acid sites in ASAs	115
7.3.2. Diversity of Brønsted acid sites in zeolites and ASAs	116
7.3.3. Grafted ASAs as a model for the variety of commercial ASAs	119
7.4. Conclusion	119
<b>8. The behaviour of amorphous aluminosilicates towards aging by high-temperature steaming</b>	
8.1. Introduction	121
8.2. Results	122
8.2.1. Adsorption of ethanol followed by thermogravimetry	122
8.2.2. <i>m</i> -xylene isomerization	123
8.2.3. Texture	124
8.2.4. NMR	125
8.2.5. CO adsorption followed by infrared spectroscopy	126
8.3. Discussion	130
8.3.1. The effect of steaming on Si/Al <sub>2</sub> O <sub>3</sub> materials	130
8.3.2. The effect of steaming on Al/SiO <sub>2</sub> materials	131
8.4. Conclusion	132
<b>Concluding remarks and Outlooks</b>	<b>133</b>
<b>References</b>	<b>135</b>
<b>Curriculum Vitae</b>	<b>141</b>
<b>List of publications</b>	<b>142</b>
<b>Conferences</b>	<b>143</b>
<b>Acknowledgments</b>	<b>145</b>