

# **Supporting Information**

## Multiscale Visualization and Quantification

### of the Effect of Binders on the Acidity of Shaped Zeolites

Koen Kennes,<sup>[a,b]</sup>, Alexey Kubarev,<sup>[a]</sup> Coralie Demaret,<sup>[b]</sup> Laureline Treps,<sup>[b]</sup> Olivier Delpoux,<sup>[b]</sup> Mickael Rivallan,<sup>[b]</sup> Emmanuelle Guillon,<sup>[b]</sup> Alain Méthivier,<sup>[b]</sup> Theodorus de Bruin,<sup>[c]</sup> Axel Gomez,<sup>[b,d]</sup> Bogdan Harbuzaru,<sup>[b]</sup> Maarten B.J. Roeffaers\*<sup>[a]</sup> and Céline Chizallet\*<sup>[b]</sup>

[a] Centre for Membrane separations, Adsorption, Catalysis and Spectroscopy for sustainable solutions, Faculty of Bioscience Engineering, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium

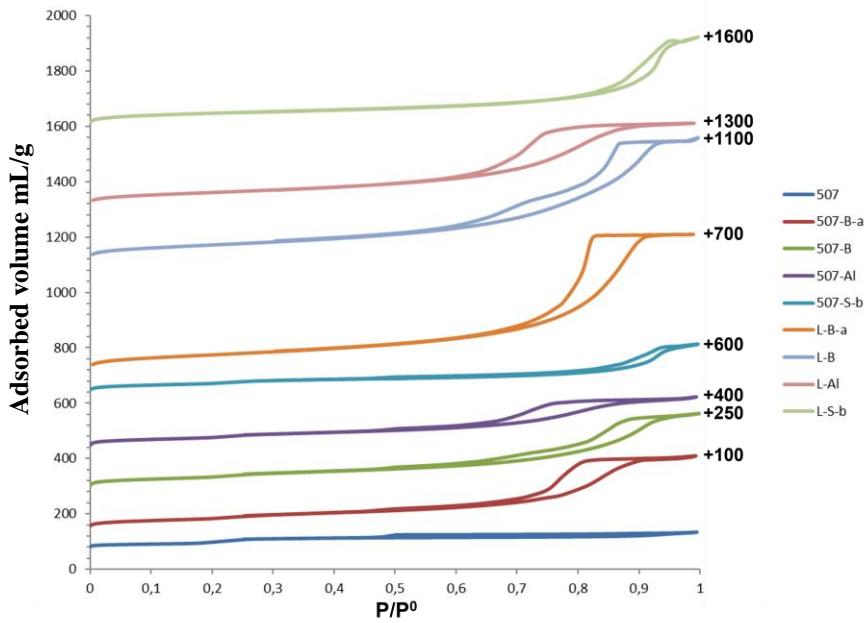
[b] IFP Energies nouvelles – Rond-Point de l’Echangeur de Solaize – BP 3 69360 Solaize, France

[c] IFP Energies nouvelles, 1 et 4 avenue de Bois-Préau, BP3, 92852 Rueil-Malmaison, France

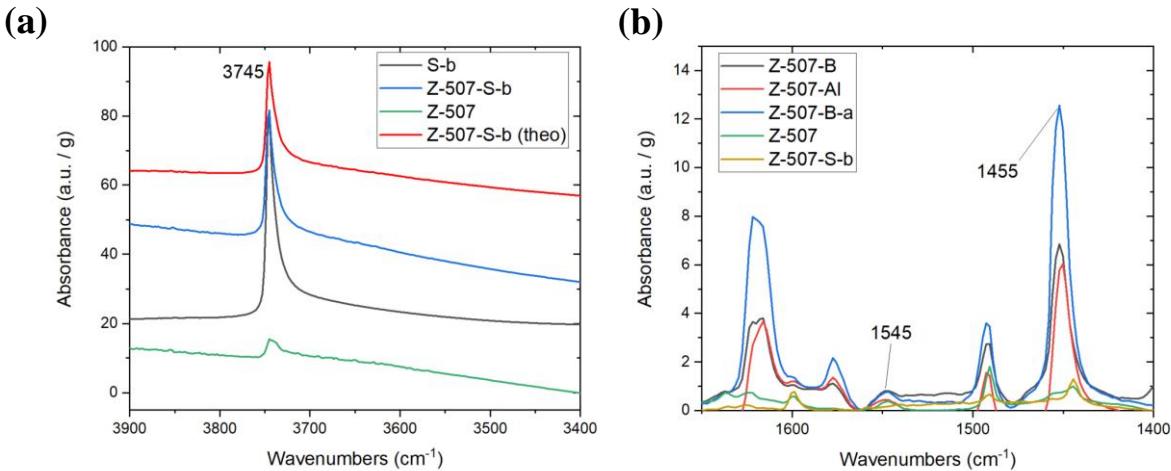
[d] Département de Chimie, École Normale Supérieure, PSL University, 75005 Paris, France

[maarten.roeffaers@biw.kuleuven.be](mailto:maarten.roeffaers@biw.kuleuven.be)

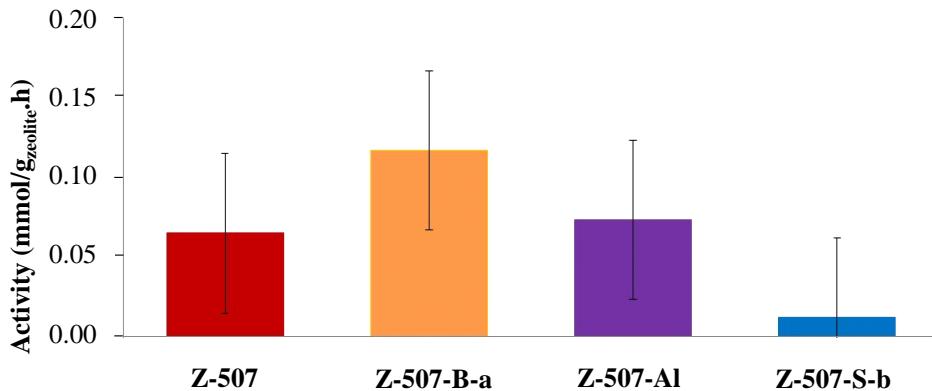
[celine.chizallet@ifpen.fr](mailto:celine.chizallet@ifpen.fr)



**Figure S1.** N<sub>2</sub> adsorption isotherms of the investigated samples. For the sake of clarity, the Y axe is offset by the amount given on the right.



**Figure S2.** IR spectra of Z-507 based samples, (a) in the hydroxyl region, (b) after Pyridine thermodesorption at 423 K in the v(CN) region.



**Figure S3.** Activity of the samples in meta-xylene isomerization test.

**Table S1.** Adsorption energies of the alumina and silica monomers in ZSM-5 bulk in kJ mol<sup>-1</sup>.

Monomer	Zeolite site	Bond	Proton transfer	Site name	$\Delta_{ads} U_{monomer}$ (kJ mol <sup>-1</sup> )
Al	Al	Covalent	Yes	A	-194
					-198
			No	B	-151
					-111
					-167
		Hydrogen bond	Yes	C	-186
					-182
					-192
					-219
					-148
					-166
					-149
					-191
					-238
			No	D	-106
					-131
					-90
					-117
					-106
Al(OH) <sub>3</sub> (H <sub>2</sub> O)	Si	Covalent	No	E	-85
					-106
					-85
					-106
		Hydrogen bond	No	F	-114
					-85
					-95
					-105
					-86
					-92
					-88
					-99
					-80
					-89
					-81
					-88
					-78
					-89
					-80
					-93
					-79
					-91
					-70
					-74
					-88
					-85
					-81
					-66
					-82
					-96
					-85
					-76
					-81
					-80
					-86
					-76
					-89
					-79
					-83

					-79
					-87
					-78
					-85
		Covalent	No	G	-101
					-109
	Al	Hydrogen bond	Yes	H	-140
					-148
	Si	Hydrogen bond	No	I	-120
					-154
					-138
					-139
					-130
				J	-75
					-81
					-78
					-76
					-75
	Si	Hydrogen bond	No	K	-72
					-74
					-76
					-75
					-62
					-72
					-71
					-72
					-75
					-70
					-77
					-77
					-77
					-80
					-77

**Table S2.** Alumina and silica monomer adsorption representations in bulk of ZSM-5 depending on the nature of the monomer, the adsorption site and the bond formed. (a) Ball and stick representation of the most stable monomer and the adsorption site (b) Adsorption energies of the alumina and silica monomers in ZSM-5 bulk in  $\text{kJ mol}^{-1}$ , the position corresponding to the ball and stick view is underlined (c) On these structures, the adsorption reaction is a condensation reaction, the adsorption energy is calculated using the following equation:  $\Delta_{\text{ads}}U_{\text{monomer}}=U_{\text{surf\_monomer}}+U_{\text{water}}-U_{\text{surf}}-U_{\text{monomer}}$ .

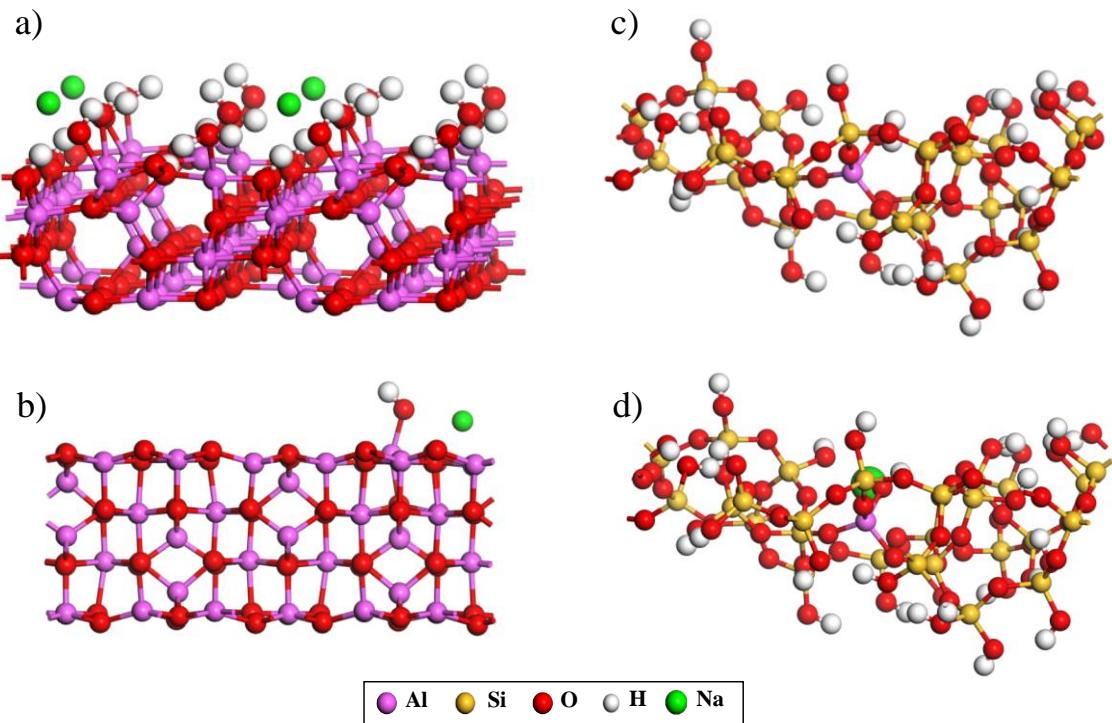
Monomer	Category	External surface aluminated site	Ball and stick view <sup>(a)</sup>	Description of the adsorption modes	$\Delta_{\text{ads}}U_{\text{monomer}} (\text{kJ mol}^{-1})$ <sup>(b)</sup>
$\text{Al(OH)}_3(\text{H}_2\text{O})$	Covalent Bond with aluminated site	No. 59 $\text{Al}(\text{H}_2\text{O})$		Covalent bond, Si-OH-Al break	-147
				2MR with two aluminum atoms <sup>(c)</sup>	<u>-170</u>
				Covalent bond, hydrogen bond with the water molecule <sup>(c)</sup>	-146
				Covalent bond, no hydrogen bond with the water molecule <sup>(c)</sup>	-108
				Hydrogen Bond and proton transfer	-115
	Hydrogen Bond and proton transfer, with aluminated site	No. 59 $\text{Al}(\text{H}_2\text{O})$		Hydrogen Bond and proton transfer	-104
				Surface site: $\text{Al}(\text{H}_2\text{O})$	-87
				Surface site: proton transferred to a Si-O-Al bridge	-241
				Surface site: proton transferred to a Si-O-Al bridge	-193
				Surface site: proton transferred to a Si-O-Al bridge	-205
	Hydrogen Bond with aluminated site	No. 59 $\text{Al}(\text{H}_2\text{O})$		Hydrogen Bond and proton transfer	-199
				Hydrogen Bond and proton transfer	-249
				Hydrogen Bond and proton transfer	-206
				Hydrogen Bond and proton transfer	-180
				Hydrogen Bond and proton transfer	-142
	Hydrogen Bond with aluminated site	No. 59 $\text{Al}(\text{H}_2\text{O})$		Surface site: $\text{Al}(\text{H}_2\text{O})$	-197
				Surface site: $\text{Al}(\text{H}_2\text{O})$	-210
				Surface site: proton transferred to a Si-O-Al bridge	-136
	Hydrogen Bond with aluminated site	No. 59 $\text{Al}(\text{H}_2\text{O})$		Surface site: proton transferred to a Si-O-Al bridge	-142
				Surface site: proton transferred to a Si-O-Al bridge	<u>-145</u>

					-131
		No. 59 Al(H <sub>2</sub> O)		(c)	-79 -87 -98 <u>-57</u> -47 -36 -48 -38 -79
	Covalent Bond	No		(c)	-63 -49 -46 -59 -46 -49
Al(OH) <sub>3</sub> (H <sub>2</sub> O)		No		Hydrogen bonds with water <sup>(c)</sup>	<u>-92</u> -79
		No. 59 Al(H <sub>2</sub> O)		Si pentavalent	-81
	Hydrogen Bond	No			-75 -72 <u>-77</u> -71
					-92 <u>-97</u>
				Hydrogen bonds with water	-117 <u>-148</u> -142 -135

					-66
$\text{Si}(\text{OH})_4$	Covalent Bond with aluminated site	No. 59 $\text{Al}(\text{H}_2\text{O})$		(c)	-86
					-24
					-65
					-72
					-127
	Hydrogen Bond with aluminated site	No. 59 $\text{Al}(\text{H}_2\text{O})$		Surface site: $\text{Al}(\text{H}_2\text{O})$	-117
					-114
				Surface site: proton transferred to a $\text{Si}-\text{O}-\text{Al}$ bridge	-101
					-117
					-75
	Covalent Bond	No. 59 $\text{Al}(\text{H}_2\text{O})$		Covalent bond on Si second neighbor of aluminated site <sup>(c)</sup>	-46
					-56
		No		Covalent bond not neighboring the aluminated site <sup>(c)</sup>	-27
					-37
					-39
	Hydrogen Bond	No. 59 $\text{Al}(\text{H}_2\text{O})$		(c)	-48
					-58
					-41
					-71
					-71
		No			-71
					-69
					-78
					-52
					-84
					-96

**Table S3.** Exchange energies (kJ/mol, calculated according to eq. (1) in the manuscript) between zeolite and binder models. For one cation adsorbed on a model various position are explored and the most stable of these positions are included in the calculations.

Zeolite/binder model	Silica	Aluminated silica	Alumina (100)	Alumina (110)
ZSM-5 bulk	-63	-27	-45	-117
ZSM-5 external surface	-27	8	-9	-81



**Figure S4.** Models of sodium-exchanged alumina: a) (110) surface, b) (100) surface, and models of aluminated silica, c) proton exchanged, d) with one proton exchanged by sodium.