## **SUPPORTING INFORMATION**

# Spectroscopic Expression

## of the External Surface Sites of H-ZSM-5

Laureline Treps,<sup>1,‡</sup> Coralie Demaret,<sup>1,‡</sup> Dorothea Wisser,<sup>2,†</sup> Bogdan Harbuzaru,<sup>1</sup> Alain Méthivier,<sup>1</sup> Emmanuelle Guillon,<sup>1</sup> Denys Viktorovych Benedis,<sup>1</sup> Axel Gomez,<sup>1,3</sup> Theodorus de Bruin,<sup>4</sup> Mickaël Rivallan,<sup>1</sup> Leonor Catita,<sup>1</sup> Anne Lesage,<sup>2</sup> Céline Chizallet<sup>1,\*</sup>

<sup>1</sup> IFP Energies nouvelles – Rond-Point de l'Echangeur de Solaize – BP 3 69360 Solaize, France

<sup>2</sup> Centre de RMN À Très Hauts Champs, Université de Lyon (CNRS/ENS Lyon/UCB Lyon
1), 69100 Villeurbanne, France

<sup>3</sup> Département de Chimie, École Normale Supérieure, PSL University, 75005 Paris, France

<sup>4</sup> IFP Energies Nouvelles, 1 et 4 avenue de Bois-Préau, BP3, 92852 Rueil-Malmaison, France

\* <u>celine.chizallet@ifpen.fr</u>

### S1. Additional structural DFT data

#### S1.1. Surface orientations considered



**Figure S1**. Side views of the surface model used as a basis for the simulation of the external surface of ZSM-5: (a) (100) orientation, according to cleavages 1, 6 and 10 (see ref.  $^{1}$ , (b) (010) orientation, (101) orientation.





Figure S2. Nitrogen adsorption isotherm for the Z-22-Big (rhombus) and Z-25-Small (squares) samples.



**Figure S3.**<sup>27</sup> Al NMR spectra of the two hydrated zeolite samples.



**Figure S4.** Experimental <sup>27</sup> Al MQ-MAS NMR spectra ( $B_0 = 9.4T$ ,  $v_r = 14$ kHz) of Z-22-Big hydrated zeolite sample with F1 and F2 projections. F1 dimension corresponds to isotropic multiple-quantum dimension, while F2 corresponds to the anisotropic multiple-quantum dimension.



**Figure S5.** Experimental <sup>27</sup>Al MQ-MAS NMR spectra ( $B_0 = 9.4T$ ,  $v_r = 14$ kHz) of Z-25-Small hydrated zeolite sample with F1 and F2 projections. F1 dimension corresponds to isotropic multiple-quantum dimension, while F2 corresponds to the anisotropic multiple-quantum dimension.



**Figure S6.** Experimental <sup>27</sup>MAS NMR spectra (in blue) obtained for (a) Z-22-Big and (b) Z-25-Small in hydrated state ( $B_0 = 9.4T$ ,  $v_r = 14kHz$ ). Using DMFit software, spectral deconvolution of <sup>27</sup>Al MQ-MAS spectra allowed one to obtain the isotropic chemical shift and the quadrupolar constant for each resonance. These parameters were then use to calculated the <sup>27</sup>MAS NMR (in red), from each the relative amounts of each aluminum site were obtained.

**Table S1.** NMR parameters of Al sites calculated from the deconvolution of the <sup>27</sup>Al MQ-MAS spectra obtained for Z-22-Big and Z-25-Small using DMFit software ( $\delta_{iso}$  : isotropic chemical shift, C<sub>0</sub>: quadrupolar constant, I% relative amount of each Al site).

Al Site	Z-22-Big			Z-25-Small		
	δ <sub>iso</sub> (ppm)	C <sub>Q</sub> (kHz)	I (%)	δ <sub>iso</sub> (ppm)	C <sub>Q</sub> (kHz)	I (%)
Al <sup>VI</sup>	-0.8	834	6	-	-	-
$Al^{IV}_{1}$	54.0	1278	74	53.6	1264	43
$Al_{2}^{W}$	55.5	1183	13	55.4	1200	39
Al <sup>IV</sup> <sub>3</sub>	57.0	1315	7	57.0	1293	18

### **S3.** Additional Infrared data



**Figure S7.** FSD-IR spectra of a) Z-25-Small and b) Z-22-Big after activation at different temperatures under secondary vacuum from 423 to 723 K. In blue, difference spectrum between spectra of the sample activated at 423 and 673 K.

## S4. Additional <sup>1</sup>H NMR data

• Calculated chemical shift of protons belonging to hydrogen-bond donor groups



**Figure S8**. (a) Scheme of hydroxyl groups involved in an hydrogen bond as donor or acceptor. (b) Relation between the DFT calculated chemical shift and the hydrogen bond length for hydrogen bond donor groups, for bulk Si-(OH)-Al sites.

• Calculated chemical shifts of silanols ranked in terms of neighborhood with other silanols



**Figure S9.** <sup>1</sup>H NMR DFT calculated chemical shifts of silanols classified according to their neighborhood with other silanols, see Table S1 for terminology.

**Table S2**. <sup>1</sup>H NMR DFT calculated average chemical shifts of silanols classified according to their neighborhood with other silanols.

	Total Average (ppm)	1	2	3	4	5	6	EFSi
Isolated	1.95	1.91	No Data	No Data	2.00	1.97	1.47	1.92
H-bond acceptor	2.48	2.51	No Data	2.48	2.48	2.29	2.56	2.85
		HO SI UND OH	HOME S OF	HOMINS ON	oH Si No	HOOH	HO SIMOH	он 

#### • Effect of crystal size: Z-22-Big vs. Z-25-Small

<sup>1</sup>H NMR spectral deconvolution was done using DMFit as illustrated in Figure S7. The <sup>1</sup>H chemical shifts obtained through spectral deconvolution gathered in Table S2. The absolute and relative integrated peaks areas obtained are reported in Figure S8. Prior to <sup>1</sup>H MAS measurements, all samples were pretreated under secondary vacuum at 300°C for 10 hours and then sealed in a glass reactor.



**Figure S10.** Deconvolution of spectral components of <sup>1</sup>H MAS NMR spectra using DMFit (in blue: experimental spectrum; in red - best fitted model). For both samples, peaks were fitted using Lorentzian curves. Despite the use of the <sup>1</sup>H DEPTH sequence, a very large and weak signal can be observed around 0.9 ppm, which can be attributed to probe background signal. The intensity, width and position of this signal were kept constant for spectral deconvolution in both cases.

**Table S3.** <sup>1</sup>H chemical shifts obtained from <sup>1</sup>H MAS NMR spectral deconvolution using DMFit for Z-22-Big and Z-25-Small samples.

	Z-22-Big	Z-25-Small	
OH group	δ ( <sup>1</sup> H) / ppm	δ ( <sup>1</sup> H) / ppm	
H-bond acceptor µ <sub>1</sub> / µ <sub>2</sub> -Al-	1.3	1.4	
UH			
Isolated SiOH and Silanol-	1.9	1.8	
Al	-	2.1	
Al-(H <sub>2</sub> O) with one donor H,			
hydrogen-bond acceptor	26	2.7	
silanols and Silanol-Al, and	2.0	2.7	
μ <sub>2</sub> -Al-OH			
Bridging Si-(OH)-Al and	4 1	4.1	
isolated Al-(H <sub>2</sub> O)	4.1	4.1	
H-bond donors	5.1	4.9	



**Figure S11.** Relative peak intensity contributions obtained from deconvolution of <sup>1</sup>H MAS NMR spectra using DMFit. Note that these values have an estimated uncertainty of 10% and values below 5% are not precise.<sup>2</sup> The intensity of the peak at 0.9 ppm (probe background) was not taken into account in these calculations.

**Projections of 2D NMR** 



**Figure S12.** Projection along F1 dimension of 1H SQ-DQ spectra for the Z-25-Small sample, at a position of (a) 7.6 ppm, (b) 5.5 ppm in F1.

### References

(1) Treps, L.; Gomez, A.; De Bruin, T.; Chizallet, C., Environment, Stability and Acidity of External Surface Sites of Silicalite-1 and ZSM-5 Micro- and Nano-Slabs, -Sheets and - Crystals, *ACS Catal.* **2020**, *10*, 3297–3312.

(2) Batista, A. T. F.; Wisser, D.; Pigeon, T.; Gajan, D.; Diehl, F.; Rivallan, M.; Catita, L.; Gay, A.-S.; Lesage, A.; Chizallet, C.; Raybaud, P., Beyond  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystallite surfaces: The hidden features of edges revealed by solid-state <sup>1</sup>H NMR and DFT calculations, *J. Catal.* **2019**, *378*, 140-143.