SUPPORTING INFORMATION

S1: COSMO CALCULATION OF SOLVATION ENERGIES OF GAS PHASE XYLITOL

As a benchmark, the COSMO solvation energy was first calculated in the case of non adsorbed xylitol molecules. To the best of our knowledge, no solvation data for xylitol from the gas phase is available in the literature, whereas some data are available in the case of ethylene-glycol.[1]Table S1-1 provides COSMO calculated results for ethylene-glycol and xylitol, for two values of the water dielectric constant: 78.4 (value at 298 K, for which experimental data are available) and 60.9 (350 K, close to our own experiments), and taking into account variations in the vibrational partition functions from the vacuum to the solvated phase.

Table S1-1. Standard solvation energy and free energy of ethylene-glycol and xylitol from the gas phase to an aqueous solution, calculated by the COSMO approach, and experimental value for ethylene-glycol at 298 K (from ref. 1}).

Molecule		**Ethylene-glycol**		**Xylitol**
T (K)		298	350	350
ε for water		78.4	60.9	60.9
Calc. $\Delta_{solv}U°$ (kJ/mol)		-43.1	-42.7	-62.4
$\mu^{o}_{xy\,(T,g)} - \mu^{o}_{xy\,(T,solv)}$ **(kJ/mol)**	**Calc.**	-46.9	-55.7	-91.3
	Exp.	-38.9	-	-

It appears that the COSMO calculation for ethylene-glycol at 298 K provides $\Delta_{solv}G°$ in reasonable agreement with the experimental data and previously computed values,[2,3,4] which

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[1] Suleiman, D.; Eckert, C. A. *J. Chem. Eng. Data* **1994**, *39*, 692.

[2] Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1994**, *116*, 3892.

[3] Taylor, R. S.; Garrett, B. C. *J. Phys. Chem. B* **1999**, *103*, 844.

validates the method. Experiments also indicate that $\Delta_{solv}G°$ for ethanol is about -21 kJ/mol,[5] which could be interpreted as a solvation free energy gain of more than -20 kJ/mol per OH group in the molecule. Comparing xylitol and ethylene-glycol solvation free energies at 350 K shows that this rationale does not hold for C_5 polyols, as the solvation free energy is lower than -100 kcal/mol. This reveals the loss of solvent accessible surface due to the association of OH groups on the same molecular skeleton, consistently with the "group contribution" approach of *Cabani et al.*[6] In the paper, the -91.3 kJ/mol value is thus used for the calculation of interfacial energies.

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[4] Chambers, C. C.; Hawkins, G. D.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem.* **1996**, *100*, 16385.

[5] Ben-Naim, A.; Marcus, Y. *J. Chem. Phys.* **1984**, *81*, 2016.

[6] Cabani, S.; Gianni, P.; Mollica, V.; Lepori, L. *J. Solution Chem.* **1981**, *10*, 563.

S2: MODEL SYSTEMS FOR THE CALCULATION OF ^{13}C NMR SHIFTS

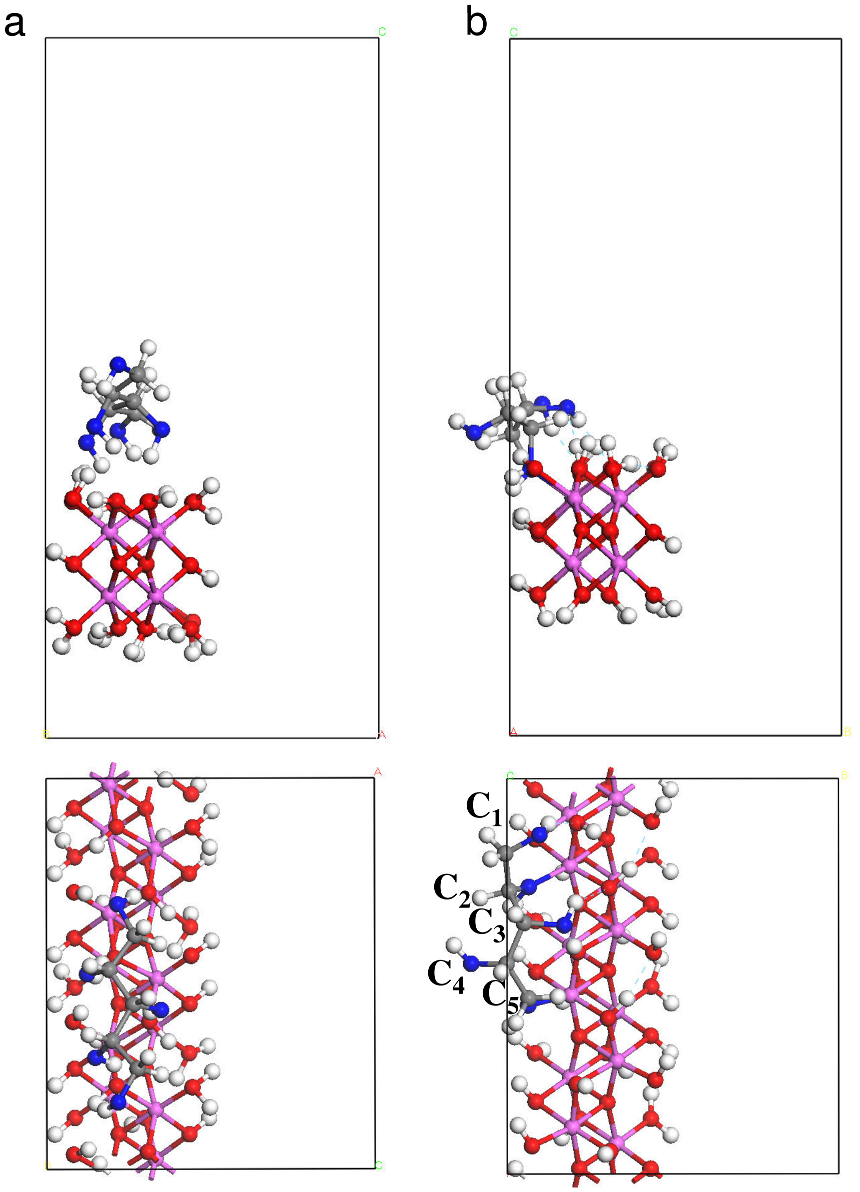

Figure S2-1: Unit cells of systems representing xylitol adsorbed on boehmite (101), reduced for the purpose of NMR calculations: (a) preferred molecular mode, (b) preferred bidentate mode (grafted on the surface trough C_2 and C_5). Same colors as Figure 9.