

## Ab Initio Screening of Cation-Exchanged Zeolites for Biofuel Purification

### Supplementary Information

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#### Contribution of dispersion (London) interactions to the adsorption of phenol, toluene and water in FAU zeolites using additive dispersion-corrected DFT schemes

In order to discuss the contribution of dispersion interactions due to London forces to the adsorption of the studied molecules, we have reported in Table S1 both interaction energies and the corresponding contribution of dispersion energies using four additive corrective schemes, D2, TS, TS/Hi and FI/MBD.

Table S1 : Interaction energies  $\Delta E_{\text{int}}$  (kJ/mol) of phenol, toluene and water on DAY, M-exchanged faujasite (Si/Al=47), LAS (Si/Al=47), and EX-LAS (Si/Al=15). The contribution of the dispersive interactions to the adsorption energies  $\Delta E_{\text{disp}}$  (kJ/mol) are reported in brackets.

$\Delta E_{\text{int}}$ ( $\Delta E_{\text{disp}}$ ) in kJ/mol			
Phenol	Phenol	Toluene	Water
(OH)interaction	( $\pi$ )interaction		
PBE+D2			

DAY	27.0 (29.3)	51.8 (58.1)	47.4 (59.7)	16.9 (13.8)
H-FAU	81.8 (42.5)	61.7 (60.7)	62.3 (64.7)	85.3 (20.4)
Li-FAU	88.8 (37.3)	104.7 (88.5)	111.1 (89.6)	81.0 (17.5)
Na-FAU	69.2 (36.9)	102.5 (73.7)	115.7 (80.1)	56.9 (8.6)
K-FAU	53.7 (22.9)	77.0 (43.3)	86.6 (52.1)	63.7 (12.7)
Cs-FAU	61.5 (43.8)	98.9 (71.6)	111.1 (85.0)	42.1 (10.9)
Cu-FAU	82.5 (35.3)	130.4 (39.5)	146.0 (65.0)	69.7 (6.7)
Ag-FAU	86.2 (33.1)	130.4 (50.4)	139.6 (58.2)	82.6 (16.9)
LAS-FAU	173.3 (45.5)	162.5 (69.5)	135.7 (72.0)	43.9 (21.8)
EX-LAS	203.8(45.6)	210.3(85.9)	185.6 (45.6)	190.1 (14.9)
PBE+TS				
DAY	34.2 (36.8)	69.9 (74.3)	66.2 (74.3)	21.3 (19.0)
H-FAU	90.6 (51.6)	77.7 (73.0)	80.8 (80.7)	82.7 (18.6)
Li-FAU	98.0 (43.4)	108.4 (78.3)	116.6 (81.0)	72.6 (7.0)
Na-FAU	80.0 (42.2)	105.8 (57.6)	122.4 (83.1)	62.3 (14.6)
K-FAU	69.7 (38.1)	95.8 (57.6)	110.6 (71.1)	67.9 (16.8)
Cs-FAU	68.1 (43.5)	84.9 (58.1)	99.3 (73.6)	39.5 (7.7)
Cu-FAU	89.8 (35.1)	147.7 (80.8)	161.4 (86.8)	74.5 (11.0)
Ag-FAU	91.6 (36.8)	146.0 (74.3)	148.4 (74.0)	85.2 (16.9)
LAS-FAU	183.4 (57.3)	175.1 (80.8)	153.1 (86.8)	43.2 (23.4)
EX-LAS	209.9 (39.2)	219.6 (55.3)	189.3 (60.3)	191.1 (8.7)
PBE+TS/HI				
DAY	29.4 (31.0)	55.0 (50.2)	54.5 (53.4)	13.1 (9.2)
H-FAU	78.8 (39.8)	58.0 (51.8)	63.4 (56.8)	74.6 (10.3)
Li-FAU	86.9 (34.5)	83.0 (51.5)	90.9 (56.8)	74.4 (10.1)
Na-FAU	74.7 (30.9)	96.7 (52.6)	109.5 (59.7)	62.0 (6.7)
K-FAU	60.4 (28.0)	81.0 (50.1)	93.3 (57.1)	58.3 (9.2)
Cs-FAU	57.7 (33.4)	68.3 (43.0)	77.9 (44.2)	38.2 (6.4)
Cu-FAU	84.4 (29.5)	138.3 (47.2)	147.2 (57.0)	67.5 (5.1)
Ag-FAU	90.4 (44.0)	131.8 (46.4)	140.1 (58.6)	78.3 (9.2)
LAS-FAU	169.2 (41.0)	151.7 (52.2)	131.0 (57.6)	33.6 (11.0)
EX-LAS	198.5 (39.6)	178.1 (55.7)	158.6 (60.8)	184.6 (8.7)
PBE+FI/MBD				
DAY	27.7 (31.6)	49.5 (50.5)	45.1 (53.8)	20.2 (18.8)

H-FAU	78.6 (38.0)	57.1 (51.5)	56.4 (53.8)	81.0 (16.3)
Li-FAU	96.2 (46.0)	86.4 (60.3)	86.4 (60.1)	82.6 (20.1)
Na-FAU	72.9 (41.2)	88.4 (59.6)	94.4 (56.2)	60.6 (12.6)
K-FAU	58.1 (27.0)	84.0 (50.4)	89.6 (53.8)	61.4 (10.5)
Cs-FAU	49.8 (27.6)	63.2 (36.9)	71.3 (45.1)	35.9 (4.1)
Cu-FAU	72.6 (18.2)	126.3 (37.0)	135.3 (51.8)	61.5 (0.4)
Ag-FAU	75.5 (21.1)	118.1 (32.1)	127.1 (44.4)	73.5 (3.8)
LAS-FAU	171.3 (43.4)	154.6 (58.2)	128.3 (53.0)	41.7 (17.9)
EX-LAS	198.5 (23.9)	178.1 (40.0)	158.6 (43.0)	184.6 (8.7)

## 1. Adsorption of phenol

### a. O-interaction

Let us now focus on the long-range dispersion energy  $\Delta E_{\text{disp}}$  calculated using the four levels of theory. This energy represents a large part of the total interaction energy  $\Delta E_{\text{int}}$  of phenol via its OH group in the cage of DAY, as the  $\Delta E_{\text{disp}}$  value ranges between 29 kJ/mol and 37 kJ/mol (See Table S1). Over the protonated site, the  $\Delta E_{\text{disp}}$  value is around 50 kJ/mol, which approximately corresponds to 50% of the total interaction energy. Over the alkali cations, the  $\Delta E_{\text{disp}}$  of phenol exhibits almost the same value using any level of theory, except for  $\text{K}^+$  where this energy is lower. So, on any given alkali metal the contribution of the dispersion energy to  $\Delta E_{\text{int}}$  is about 50%. Over  $\text{Cu}^+$ , the  $\Delta E_{\text{disp}}$  of phenol is between 18 kJ/mol and 35 kJ/mol, which gives a contribution to the total interaction energy of 25% and 50% depending on the method. However, in the Ag-FAU, D-LAS-FAU and EX-LAS-FAU, the dispersion contributions are lower than 50 %, as  $\Delta E_{\text{disp}}$  are about 34 kJ/mol, 47 kJ/mol and 37 kJ/mol, respectively.

### b. $\pi$ -interaction

In both formulation DAY, we found that the total interaction energies are mainly represented by the dispersion energy  $\Delta E_{\text{disp}}$  between 50 kJ/mol and 78 kJ/mol for DAY. This behavior can be also seen in the case of H-FAU with a  $\Delta E_{\text{disp}}$  value between 52 kJ/mol and 73 kJ/mol. In general,  $\Delta E_{\text{disp}}$  of the  $\pi$ -

interaction mode of phenol is higher than the O-interaction one. On alkali cations, this quantity has almost the same value, whatever the level of theory, which is between 50 kJ/mol and 74 kJ/mol. This quantity represents more than 60% of the total interaction energy. Therefore, the adsorption of the phenol by its aromatic ring on DAY, H-FAU and alkaline-exchanged FAU are significantly driven by the dispersion interactions [1]. However, over metal transition cations, the contribution of dispersion represents less than 40% of the total interaction energy, as the  $\Delta E_{\text{disp}}$  value ranges between 35 kJ/mol and 77 kJ/mol. Tonigold et al. [2] have studied the adsorption of some aromatic compounds such as benzene, thiophene, and pyridine on the surface of copper and silver using dispersion-corrected DFT calculations. They found that adding dispersion effects leads to adsorption energies within the range of the experimentally measured values [3]. In parallel with these findings, Ehrlich et al. [4] show that the dispersion forces are important for the intermolecular and intramolecular interactions that occur upon adsorption of aromatic molecules. On D-LAS and EX-LAS,  $\Delta E_{\text{disp}}$  exhibit values between 54 kJ/mol and 86 kJ/mol for D-LAS and between 40 kJ/mol and 86 kJ/mol for EX-LAS. Their contributions to the total interaction energy is less than 45%.

## 2. Adsorption of toluene

The energetic contributions of the long-range dispersion interactions represent the main part of the total interaction energy of toluene adsorbed in DAY, and in H-FAU  $\Delta E_{\text{disp}}$  around 64 kJ/mol. Over alkali cations, the  $\Delta E_{\text{disp}}$  value ranges between 54 kJ/mol and 77 kJ/mol, which represents more than 60% of the total interaction energy. This behavior is consistent with the one of the  $\pi$ -interaction mode of phenol. Over the transition metallic cations, the contribution of the dispersion energy generally represents less than 50% of the total interaction energy, corresponding to  $\Delta E_{\text{disp}}$  values between 48 kJ/mol and 80 kJ/mol. On both D-LAS and EX-LAS,  $\Delta E_{\text{int}}$  has a value between 43 kJ/mol and 80 kJ/mol, which means that the contribution of dispersion forces to the overall interaction is less than 40% in this case.

## 3. Adsorption of water

For the long-range dispersion interaction between water and the used faujasites, the  $\Delta E_{\text{disp}}$  represent 90 % of  $\Delta E_{\text{int}}$  in DAY, corresponding to an energetic value varying 9-19 kJ/mol for DAY. Besides, the adsorption of water over any kind of cation, namely  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Cu}^+$ , and  $\text{Ag}^+$  shows very low values of  $\Delta E_{\text{disp}}$  inferior to 20 kJ/mol, which represent low relative contributions to the total interaction energies: less than 20%. Over both D-LAS and EX-LAS, the  $\Delta E_{\text{disp}}$  is between 8.7 kJ/mol and 43.0 kJ/mol, corresponding to a contribution of dispersion to the total interaction energy between 4 % and 23 %. This explains the very small differences obtained with the four dispersion correction methods for each system except DAY and faujasite containing both D-LAS and EX-LAS (See Fig. 1 in the main manuscript).

## REFERENCES

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- 1 M.C. Tsai, E.L. Muetterties, *J. Am. Chem. Soc.*, 1982, **104**, 2534–2539.
  - 2 K. Tonigold, A. Groß, *J. chem. Phys.* 2010, **132**, 224701.
  - 3 Mei Xue , Ramesh Chitrakar , Kohji Sakane , Takahiro Hirotsu, Kenta Ooi , Yuji Yoshimura , Qi Feng, Naoto Sumida, *J. Colloid. Interface Sci.*, 2005, **285**, 487-492.
  - 4 S. Ehrlich, J. Moellmann, S. Grimme, *Acc. Chem. Res.* 2012, **46**, 916-926