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Supporting Information

L–Lysine Amino Acid Adsorption on Zeolite L: a Combined Synchrotron, X-Ray and Neutron Diffraction Study

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Supporting Information

TABLE OF CONTENTS

1.EXPERIMENTAL

1.1 Materials

The zeolite selected for the present investigation is a synthetic and commercial zeolite L purchased by Tosoh Corporation (HSZ-500KOA code) in its potassium form, with a Si_2O/Al_2O_3 equal to 6.1, Na_2O content of 0.25 wt% and surface area of 290 $m^2/g^{-1,}$ average size crystals ~63nm. L-lysine amino acid (hydrogen, L-lys, and deuterated, dL-lys) used as sorbate compounds were provided by Sigma-Aldrich (Steinheim, Germany).

The L-LTL form was exchanged with 1 M ND_4NO_3 aqueous solution for ≈140 h at room temperature in order to obtain the acidic precursor. Subsequently, the sample was filtered and heated under vacuum for 24 h at 600 °C to remove ND_3, then washed with D_2O and dried overnight at 97 °C.

1.2 Batch adsorption

The adsorption was determined by using aqueous solutions of L-Lys at different initial concentrations (in the 0.5-200 mg L-1 range), placed in contact with L zeolites with a solid/liquid ratio of 1:1 (mg/mL). The suspensions were kept at 25 °C under stirring during the contact time. The contact time was of 18 h, larger than the equilibration time determined by kinetics experiments. The pH was adjusted at 5.5 during adsorption by adding small volume of 0.1 M H_3PO_4.

To investigate the adsorption kinetics, the L-Lys uptake was measured starting from solution at concentration of 50, 75, 100 mg L^{-1}, after contact time equal to 1, 2, 5, 10, 20, 30, 45, 60 120 min. All batch experiments were carried out in triplicate. An Agilent Technologies Capillary Electrophoresis series 7100 system (Santa Clara, CA, USA) was employed to quantify L-Lys in the solution before and after the contact with zeolites. The CE system was equipped with diode array detection (DAD). For separations, extended light path (bubble cell) bare fused-silica capillaries (red G1600-61232 I.D.: 50 µm, total length: 64.5 cm, effective length: 56 cm, bubble factor: 3) obtained from Agilent Technologies (Santa Clara, CA, USA) were employed.

Hydrodynamic injection of the solutions was performed at a pressure of 10 mbar applied for 30 seconds. The detection wavelength of the CE system was 200 nm. Positive polarity (15 kV) was applied at the capillary inlet for the duration of separation. The running buffer was obtained by a 50 mM solution of Na_2HPO_4 in MilliQ water, at pH 5.5 adjusted by adding H_3PO_4. The pH of the electrolyte was measured using an AMEL pHmeter (Milano, Italy). Before use, the capillary was pretreated through sequential flushing with 1 M NaOH for 5 minutes, 0.1 M NaOH for 5 minutes and MilliQ (Millipore, Bedford, MA, USA) grade water for 15 minutes. The capillary was also rinsed with water for 3 minutes, 0.1 M NaOH for 2 minutes, water for 3 minutes, and running buffer for 5 minutes between each run.

1.3 Thermal analysis

An aliquot of L-Lys sample was placed in an alumina crucible and characterized by thermogravimetric (TG) and thermodifferential (DTA) analyses carried out in costant flux of air by means of a STA 409 PC LUXX® (Netzsch Gerätebau GmbH, Selb, Germany) simultaneous TG/DTA thermogravimetric balance from room temperature to 900 °C, with a heating rate of 10 °C/min.

1.4 Synchrotron and neutron diffraction

Data collection was carried out at the MCX (Material Characterization by X-ray Diffraction) Beamline of the Elettra Synchrotron Light Source (Trieste, Italy) on a 4-circle Huber

diffractometer equipped with a Si(111) double crystal monochromator and a high-count rate fast scintillator detector preceded by a pair of slits with vertical aperture of 200 and 300 μm. The sample was loaded into an axially spinning borosilicate capillary (Ø=0.5 mm) and then collected at room temperature, using a fix wavelength equal to 0.82700(1) Å (*i.e.*, 15 keV), in the 1.5-65° 2θ range.

Data from neutron diffraction were collected at the Institut Laue-Langevin (ILL) using the high-resolution two-axis diffractometer D2B with Ge(335)-monochromated constant-wavelength radiation (λ=1.594 Å) in Debye–Scherrer geometry. The sample was placed in a vanadium cylinder with a diameter of 8 mm, then neutron diffraction data collection was performed at 1.5 K in the 4-161° 2θ range with a step of 0.02°.

1.5 Rietveld structure refinements

Rietveld refinements from both X-ray and neutron diffraction data were performed through the GSAS-EXPGUI[1,2] software package, starting from the structural model reported by Gigli et al. (2013)[3]. Peaks profile was modelled through a Pseudo-Voigt function with 0.01% cut-off peak intensity for both collected histograms. Two Gaussian (*GW* and *GU*) and one Lorentzian (*LX*) terms, plus an anisotropic Lorentian contribution (*stec* parameter), were refined coefficients profile pattern collected at the synchrotron facility, whereas three Gaussian (*GW*, *GU* and *GV*) and one Lorentzian (LX) terms, and the *asym* parameter were used to model data derived from neutron diffraction. The background was empirically fitted though a 18 polynomial coefficients Chebyschev function. Besides, scale factor and 2θ zero shift were also refined for both the histograms. A set of soft constraints were initially imposed on bond distances for tetrahedral sites (*i.e.*, T–O=1.62 Å, σ=0.04 Å) and the organic molecule (C–C=1.54 Å, C–O=1.43 Å; C=O=1.25 Å), and completely removed in the last refinement cycles. Finally, atomic coordinates, atom site fraction, and Atomic Displacement Parameters (ADPs, Uiso) were refined. ADPs for atoms hosted at the same coordination site (*i.e.*, those at tetrahedral sites, framework oxygen atoms, and organic molecules) were imposed to be equal and constrained to change identically. Details about data collection and refinement agreement indices (*R*-values) are reported in Table 1SI. The different orientations of aminoacid are reported in Figure 1SI.

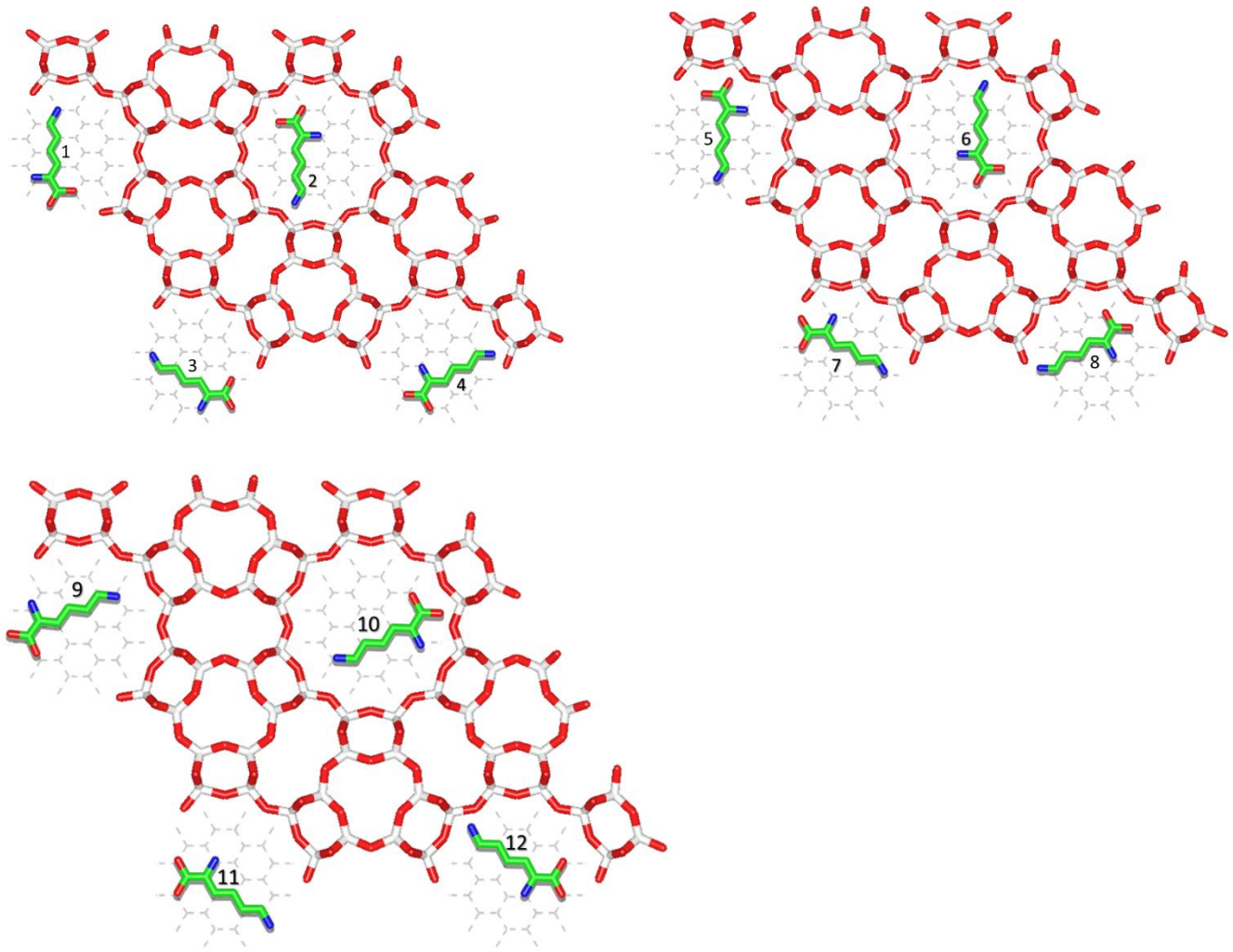


Figure1SI. Projection along the c axis of the lysine coronene-like structure. Green line: C atoms; red line: oxygens of lysine; blue line: nitrogen atoms.

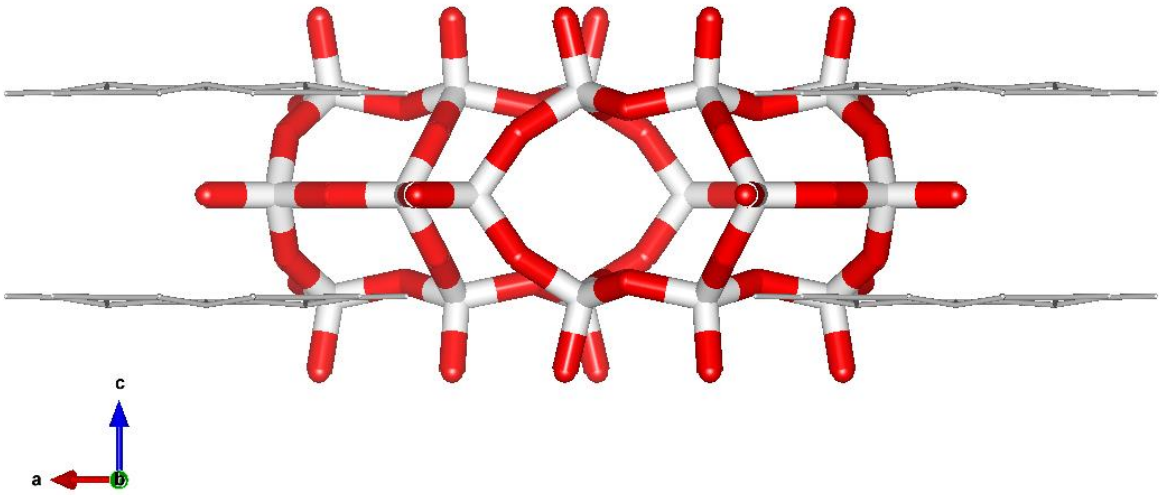


Figure2SI. Projection along the b axis of the lysine coronene-like structure. Green line: C and N atoms; red line: oxygens of lysine; white line: Si atoms.

Table 1SI.

Details of synchrotron X-ray and neutron data collection and refinements agreement indices (*R*-values).

Parameters	Synchrotron X-ray diffraction	Neutron diffraction
Wavelength (Å)	0.82700(1) Å	1.59432(1) Å
2*θ* range (°)	1.5-65	4-146
N_{data}	10596	2917
N_{obs}	1068	891
R_{wp} (%)	9.8	2.96
R_p (%)	9.7	2.11
R_F^2 (%)	10.93	12.28

$\boldsymbol{R_p = \sum[Y_{io} - Y_{ic}]/\sum Y_{io}}$; $\boldsymbol{R_{wp} = [\sum wi(Y_{io} - Y_{ic})^2/\sum wiY_{io}^2]^{0.5}}$; $\boldsymbol{R_F^2 = \sum |F_o^2 - F_c^2|/|F_o^2|}$

Atomic coordinates, atomic site fraction, and ADPs of framework atoms derived from structural refinements of data from X-ray and neutron diffraction are reported in Table 2SI and 3SI, respectively. Atomic coordinates and atomic site fraction of extraframework atoms are reported in Table 4SI.

Table 2SI.

Atomic coordinates, atomic fraction and ADPs of framework atoms obtained through structural refinement of data from synchrotron X- ray diffraction.

Site	x/a	y/b	z/c	Fraction	Multiplicity	Ui/Ue*100
KB	2/3	1/3	1/2	1.0(1)	2	4.72(2)
KC	1/2	0.0	1/2	0.70(1)	3	3.32(2)
KD	0.2917(17)	0.0	0.0	0.71(1)	6	5.17(3)
Al1	0.0938(3)	0.3576(3)	1/2	0.30	12	0.56(2)
Si1	0.0938(3)	0.3576(3)	1/2	0.70	12	0.56(2)
Si2	0.1656(2)	0.4994(2)	0.2089(2)	0.78	24	0.56(2)
Al2	0.1656(2)	0.4994(2)	0.2089(2)	0.22	24	0.56(2)
O1	0.0	0.2735(5)	1/2	1.0	6	1.16(3)
O2	0.1630(3)	0.3260(5)	1/2	1.0	6	1.16(3)
O3	0.2648(2)	0.5295(4)	0.2518(9)	1.0	12	1.16(3)
O4	0.1026(3)	0.4128(2)	0.3212(5)	1.0	24	1.16(3)
O5	0.4400(2)	0.8800(3)	0.2475(8)	1.0	12	1.16(3)
O6	0.1419(4)	0.4711(4)	0.0	1.0	12	1.16(3)

Table 3SI.

Atomic coordinates, atomic fraction and ADPs of framework atoms obtained through structural refinement of data from neutron diffraction.

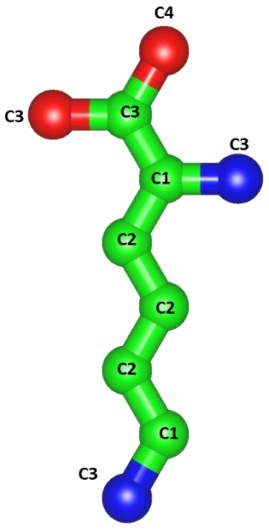
Site	x/a	y/b	z/c	Fraction	Multiplicity	Ui/Ue*100
KB	2/3	1/3	1/2	1.0(1)	2	1.26(3)
KC	1/2	0.0	1/2	0.70(1)	3	1.37(1)
KD	0.2915(35)	0.0	0.0	0.71(1)	6	1.68(3)
Al1	0.0941(7)	0.3588(8)	1/2	0.30	12	0.44(2)
Si1	0.0941(7)	0.3588(8)	1/2	0.70	12	0.44(2)
Si2	0.1664(8)	0.5012(8)	0.2089(13)	0.78	24	0.44(2)
Al2	0.1664(8)	0.5012(8)	0.2089(13)	0.22	24	0.44(2)
O1	0.0	0.2806(9)	1/2	1.0	6	1.45(3)
O2	0.1664(6)	0.3328(13)	1/2	1.0	6	1.45(3)
O3	0.2654(5)	0.5308(9)	0.2550(23)	1.0	12	1.45(3)
O4	0.1077(7)	0.4157(6)	0.3241(8)	1.0	24	1.45(3)
O5	0.4377(2)	0.8755(5)	0.2546(20)	1.0	12	1.45(3)
O6	0.1505(11)	0.4784(8)	0.0	1.0	12	1.45(3)

Table 4SI.

Atomic coordinates and atomic fraction of extraframework atoms from data of both synchrotron X- ray and neutron diffraction**.**

Site	x/a	y/b	z/c	Fraction	Multiplicity	Ui/Ue*100
C1	0.1321(12)	0.0	0.1880(27)	0.164	12	4.80(1)
C2	0.0675(3)	0.0	0.1980(19)	0.164	12	4.80(1)
C3	0.1967(30)	0.1330(15)	0.2100(9)	0.082	24	4.80(1)
C4	0.2048(40)	0.2672(33)	0.2132(10)	0.082	24	4.80(1)
W1	0.0	0.1947(2)	0.0	0.50(1)	6	4.75(1)
W2	0.0770(7)	0.1540(14)	1/2	0.87(1)	6	4.06(1)
D	0.0	0.2263(11)	1/2	0.23(1)	6	5.30(1)

Table 5SI. Lysine content estimated from Rietveld structure refinement.

Site	Atom type	Fraction	Multeplicity	a.u.c.*	Orientation
C4	O	0.082	24	1.968~2.0	
C3	O	0.082	24	1.968~2.0	
C3	C	0.082	24	1.968~2.0	
C1	C	0.164	12	1.968~2.0	
C3	N	0.082	24	1.968~2.0	
C2	C	0.164	12	1.968~2.0	
C2	C	0.164	12	1.968~2.0	
C2	C	0.164	12	1.968~2.0	
C1	C	0.164	12	1.968~2.0	
C3	N	0.082	24	1.968~2.0	

Total C atoms=12; total O atoms=4; total N atoms=4

Chemical Formula from Rietveld refinement: 2 ($C_6H_{14}N_2O_2$)

Hydrogen atoms are not considered in this calculation.

**a.u.c.= atoms per unit cell= fraction * Multeplicity*

Table 6SI

T–O bond distances and *T*–O–*T* bond angles from structure refinements of data from synchrotron X-ray and neutron diffraction.

Bond distances (Å)	Synchrotron X-ray	Neutron
***T*1–O1**	1.644(5)	1.606(1)
***T*1–O2**	1.643(2)	1.625(1)
***T*1–O4 [x2]**	1.644(3)	1.626(7)
<*T*1–O>	1.643(3)	1.620(4)
***T*2–O3**	1.653(4)	1.656(1)
***T*2–O4**	1.658(4)	1.641(1)
***T*2–O5**	1.723(3)	1.686(3)
***T*2–O6**	1.644(3)	1.614(1)
<*T*2–O>	1.669(4)	1.649(2)
***T*–O–*T* angles (°)**		
***T*1–O1–*T*1**	130.7(6)	137.7(3)
***T*1–O2–*T*1**	144.4(7)	150.4(5)
***T*2–O3–*T*2**	139.0(4)	138.2(3)
***T*1–O4–*T*2**	144.7(4)	149.4(8)
***T*2–O5–*T*2**	126.0(4)	126.3(9)
***T*2–O6–*T*2**	145.8(4)	153.7(1)
<*T*–O–*T*>	138.4(5)	142.6(5)

2. RESULTS AND DISCUSSION

2.1 Adsorption experiments

The amount of Lys adsorbed at equilibrium, q_e (mg g^{-1}), was calculated from the mass balance equation, Eq.1:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i and C_e (mg L^{-1}) are the liquid-phase concentrations of Lys in the reference solution and at equilibrium respectively; V (L) is the volume of the solution and M (g) is the mass of dry zeolite used. Samples of saturated zeolite with Lys were used for structural investigations. Zeolite L (0.5 g) were suspended with stirring in 500 ml of an aqueous solution of Lys 500 mg

L^{-1}, at pH 5.5 at 25 °C for 24 h. The zeolite was recovered by filtration, washed with 200 mL of MilliQ water and dried in oven at 300 K overnight. A similar procedure was employed to prepare the samples saturated with deuterated Lys (dL-Lys), in such a case dL-Lys was dissolved in D_2O at concentration of 1000 mg L^{-1}.

To quantify the kinetic constant, a pseudo second order (PSO) model was employed to model the data. The PSO equation is given by Eq.2:

$$q_t = \frac{k_2\ q_e^2\ t}{1+k_2\ q_e\ t} \quad (2)$$

where q_t, is the adsorbed quantity per unit mass of adsorbent after a contact time t, and k_2 is the pseudo second order kinetic constant that was employed. PSO was chosen as kinetic model since it has been reported in the literature that it can better represent the kinetics of adsorption onto zeolites with respect to both neutral and cationic species.

The adsorption data (Figure 1b in the manuscript) obtained at 25 °C were fitted to a Langmuir model, Eq.3:

$$q_e = \frac{q_s\ b\ C_e}{1 + b\ C_e} \quad (3)$$

where q_s is the saturation capacity of the zeolite and b is the binding constant; the estimated parameters with the confidence limits calculated at 95% of probability are reported in Table 5 of the manuscript.

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