Supplementary Information

The structure and location of 18-crown-6 ether in zeolites RHO and ZK-5.

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Thermogravimetry

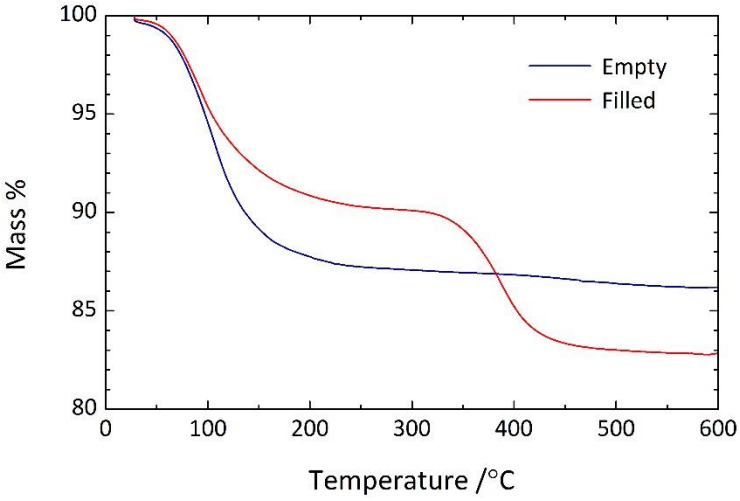

Figure S1. Thermogravimetric curves for the empty (blue) and filled (red) zeolite RHO samples. The filled sample shows two mass loss events corresponding to dehydration followed by 18C6 decomposition. The empty sample only shows the dehydration event.

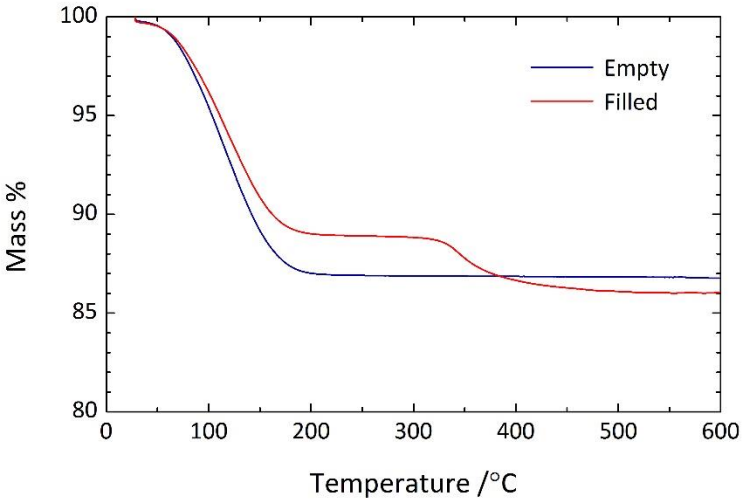

Figure S2. Thermogravimetric curves for the empty (blue) and filled (red) zeolite ZK-5 samples. The filled sample shows two mass loss events corresponding to dehydration followed by 18C6 decomposition. The empty sample only shows the dehydration event.

Zeolite RHO Refinement Procedure

Regarding both the empty and filled zeolite RHO samples, the 2θ = 2.0-45.0° data range from the diffraction patterns was used, as this included all the Bragg peaks observed in the scan range. The refinement process used 100,000 iterations and a χ^2 convergence criteria of 0.001. For ease, the Si and Al sites in the frameworks were assumed to have the same crystallographic position and the same atomic displacement parameter B_{eq}. Si and Al sites at the same crystallographic position were constrained so that the sum of their fractional occupancies was equal to 1.0. The fractional occupancy of the Si sites were further constrained between 0.78-0.80, as this agrees with the Si/Al ratio determined by EDX and SS MAS NMR, as well as anticipated for zeolite RHO.[1] The atomic displacement parameter of sites with the same element identity were constrained to be equivalent to one another, unless otherwise stated.

Empty Zeolite RHO

The starting source structure for the refinements used was the crystal structure of dehydrated zeolite RHO in the $I\bar{4}3m$ symmetry reported by Parise *et al.*[2] The modified Thompson-Cox-Hastings pseudo-Voigt (TCHZ) peak shape was used to perform the refinements. The final refined profile functions were: pku = 0.7-1(13), pkv = -0.0008(27), pkw = 0.0(12), pkz = 0.0(12), pky = 0.20(1) and $pkxz$ = 0.009(1). A total of fifteen background functions were used.

The extra-framework cations were added to the structural model sequentially. The crystallographic coordinates for the Cs and Na sites were not refined as both exist at special positions. An X-ray adsorption factor for the Cs site was included, being refined to: ADPs = 0.0319(5). The fractional occupancy of both cation sites were constrained with 1.0 as a maximum. The x and y coordinates for site O(1) were constrained to be equivalent. The same was done for site O(2). Figure S3 shows the final refined unit cell structure of the empty zeolite RHO.

Filled Zeolite RHO

The final refined empty zeolite RHO structure determined herein was used as the starting source structure for the filled zeolite RHO refinements. The modified TCHZ peak shape was again used to perform the refinements. The final refined profile functions were: pku = -0.24(1), pkv = 0.085(9), pkw = 0.000(4), pkz = 0.000(4), pky = 0.237(4) and $pkxz$ = 0.0058(2). A total of thirteen background functions were used.

The crystallographic coordinates of the Cs site were not refined as it exists at a special position. An X-ray adsorption factor for the Cs site was included, being refined to: ADPs = 0.0364(4). The position of the Na site was refined, with the x, y and z coordinates being constrained as equivalent. The same constraints on the x and y coordinates for sites O(1) and O(2) used for the empty zeolite RHO refinement were used.

The occluded 18C6 species was modelled as a rigid body, using a z-matrix construction of the Cartesian coordinates of a geometry optimised 18C6 species used previously by Nearchou *et al.*[3] The 18C6 oxyethylene chain was in the D_{3d} conformation, with a dummy "X" atom included in the centre of the 18C6 cavity, located in the centre of the α-cage at ½x, ½y, ½z. The "X"-O distances were 2.815-2.816 Å, the C-O distances 1.425-1.426 Å and the C-C distances 1.513-1.514 Å. The refined atomic coordinates of the 18C6 species were obtained by refining the rotation and translation of the rigid body. The fractional occupancy of the C and O sites in the 18C6 species were constrained to be equivalent, to give an occupancy of the entire rigid body. The atomic displacement parameters of the C and O sties were also constrained to be equivalent. Attempts to refine the occupancy of a Na

or Cs cation at the "X" dummy site in the centre of the 18C6 cavity demonstrated that this site was not occupied.

For all sites in the structure, the fractional occupancy was constrained with 1.0 as a maximum. Figure S4 shows the final refined unit cell structure of the filled zeolite RHO.

Zeolite ZK-5 Refinement Procedure

Regarding both the empty and filled zeolite ZK-5 samples, the 2θ = 5.0-100.0° data range from the diffraction patterns was used, as this included all the Bragg peaks observed in the scan range. The refinement process used 100,000 iterations and a χ^2 convergence criteria of 0.001. For ease, the Si and Al sites in the frameworks were assumed to have the same crystallographic position and the same atomic displacement parameter B_{eq}. Si and Al sites at the same crystallographic position were constrained so that the sum of their fractional occupancies was equal to 1.0. The fractional occupancy of the Si sites were further constrained between 0.79-0.82, as this agrees with the Si/Al ratio determined by EDX and anticipated for zeolite ZK-5.[1] The atomic displacement parameter of sites with the same element identity were constrained to be equivalent to one another, unless otherwise stated.

A zeolite W/merlinoite impurity based on the structure reported by Galli *et al.*[4, 5] was included for both the empty and filled zeolite ZK-5 refinements.

<u>Empty Zeolite ZK-5</u>

The starting source structure for the refinements used was the crystal structure of zeolite ZK-5 in the $Im\bar{3}m$ symmetry reported by Parise *et al.*[6] The only adjustment made in the starting structure was that the Cs site was substituted with a K site. The modified Thompson-Cox-Hastings pseudo-Voigt (TCHZ) peak shape was used to perform the refinements. The final refined profile functions were: pku = 0.1(2), pkv = 0.010(3), pkw = 0.0(2), pkz = 0.0(2), pky = 0.109(6) and pkx = 0.028(1). A total of fourteen background functions were used.

The extra-framework cations were added to the structural model sequentially. This was then followed by the addition of the water oxygen Ow sites into the structure. The crystallographic coordinates of both sites K(1) and K(2) were not refined as both exist at special positions. Both the x and y coordinates of site K(3) were fixed at 0.0. The x and y coordinates for site O(1) were constrained to be equivalent. The same was done for site O(2). The x coordinates of sites O(3) and O(4) were constrained to be equivalent to 0 and 0.5 respectively. The sum of the y and z coordinates of site O(4) were constrained to equal 0.5. For site Ow(1) the y and z coordinates were fixed at 0.0 and 0.5 respectively. The crystallographic coordinates for site Ow(2) were not refined as it was seen to exist at a special position. Regarding site Ow(3) all three coordinates were constrained to be equivalent. For the Ow(4) site, both the x and y coordinates were fixed at 0.0. The fractional occupancy of all the cation and Ow sites were constrained with 1.0 as a maximum. The sum of the fractional occupancies of sites K(2) and Ow(3) were constrained to be equal to 1. Figure S5 shows the final refined unit cell structure of the empty zeolite ZK-5.

<u>Filled Zeolite ZK-5</u>

The final refined empty zeolite ZK-5 structure determined herein was used as the starting source structure for the filled zeolite ZK-5 refinement. The modified TCHZ peak shape was again used to perform the refinements. The final refined profile functions were: pku = 0.06(5), pkv = 0.014(2),

pkw = 0.00(5), pkz = 0.0(5), pky = 0.020(5) and pkx = 0.0262(7). A total of fourteen background functions were used.

The K(1)and K(3) extra-framework cation sites, and Ow(1), Ow(3) and Ow(4) water oxygen sites were subjected to the same constraints on their crystallographic coordinates as was performed on the refinement of the empty zeolite ZK-5. Site K(2) was removed, as during the refinement process this site was seen to not be occupied. Site Ow(2) was also removed, due to being located in the same position as part of the modelled 18C6 species.

The occluded 18C6 species was modelled in the same way as was performed for the filled zeolite RHO, using the same rigid body constructed from the geometry optimised 18C6 species used previously by Nearchou *et al.*[3] The refined atomic coordinates of the 18C6 species were obtained by refining the rotation and translation of the rigid body. The fractional occupancy of the C and O sites in the 18C6 species were constrained to be equivalent, to give an occupancy of the entire rigid body. The atomic displacement parameters of the C and O sties were also constrained to be equivalent. The dummy "X" atom at the centre of the 18C6 cavity was refined as site K(4), with the fractional occupancy and atomic displacement parameter refined. The position of site K(4) was not refined as it exists at a special position.

For all sites in the structure, the fractional occupancy was constrained with 1.0 as a maximum. Figure S6 illustrates the final refined unit cell structure of the filled zeolite ZK-5.

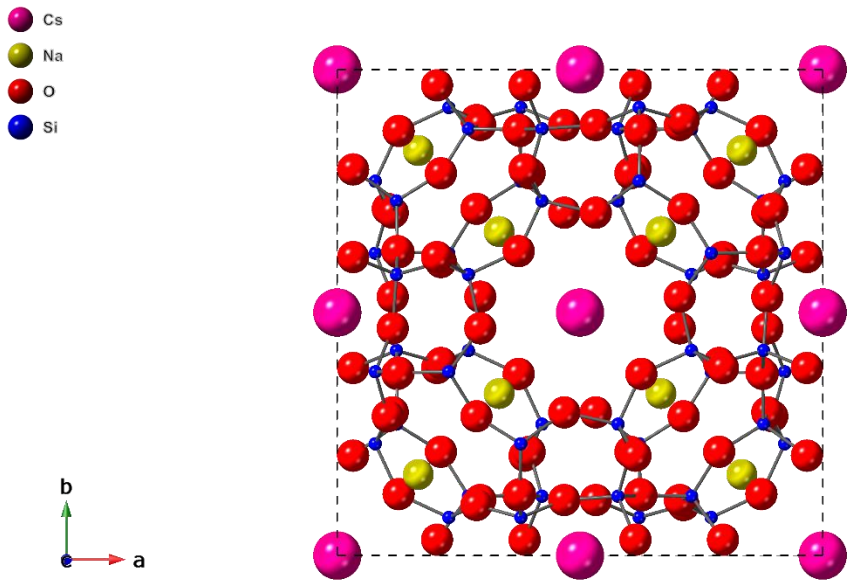

Figure S3. Final refined unit cell structure for the empty zeolite RHO sample. Viewed down the a axis. T atoms (Si and Al) are shown as blue spheres, oxygen atoms as red spheres, sodium cations as yellow spheres and caesium cations as pink spheres.

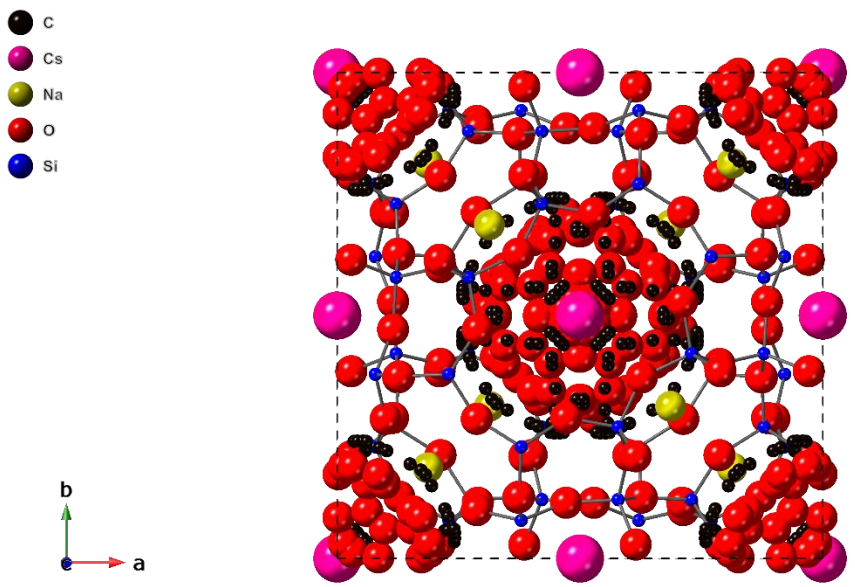

Figure S4. Final refined unit cell structure for the filled zeolite RHO sample. Viewed down the a axis. T atoms (Si and Al) are shown as blue spheres, oxygen atoms as red spheres, carbon atoms as black spheres, sodium cations as yellow spheres and caesium cations as pink spheres.

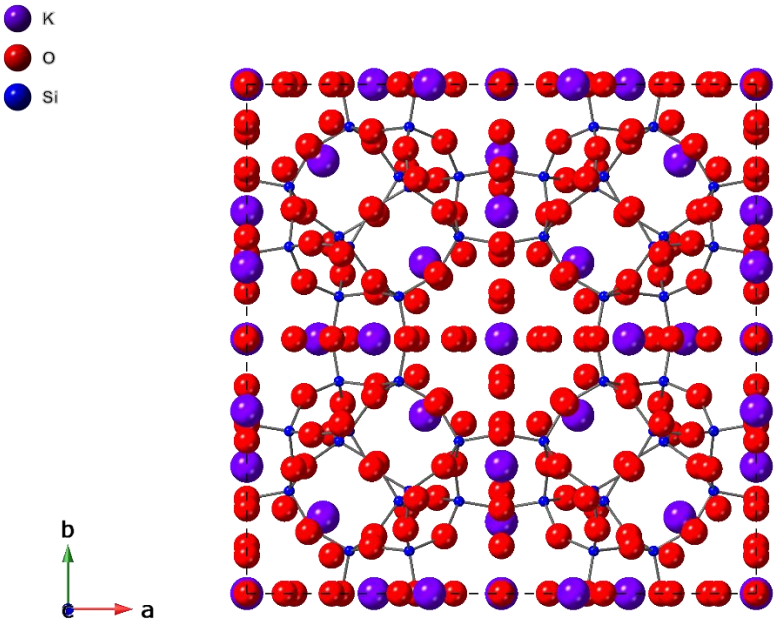

Figure S5. Final refined unit cell structure for the empty zeolite ZK-5 sample. Viewed down the a axis. T atoms (Si and Al) are shown as blue spheres, oxygen atoms as red spheres and potassium cations as purple spheres.

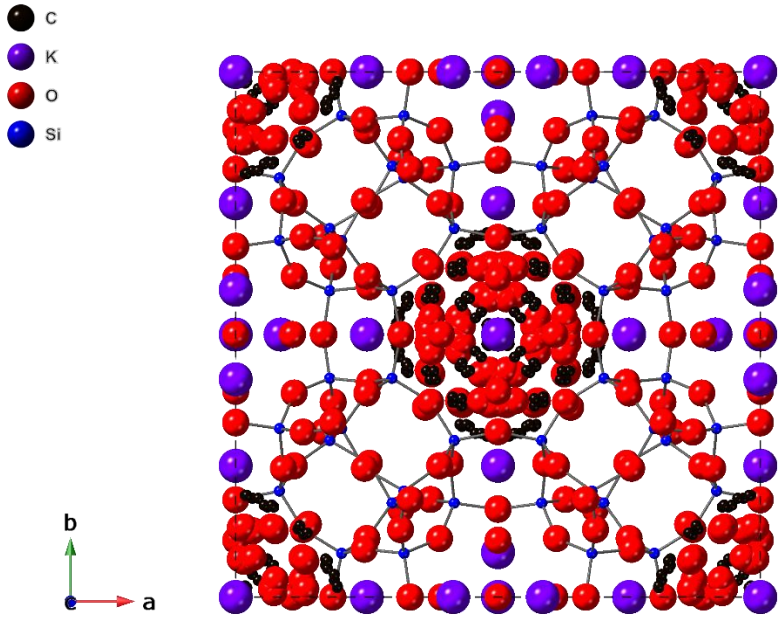

Figure S6. Final refined unit cell structure for the filled zeolite ZK-5 sample. Viewed down the a axis. T atoms (Si and Al) are shown as blue spheres, oxygen atoms as red spheres, carbon atoms as black spheres and potassium cations as purple spheres.

Bibliography

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