Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting information

Index:

1 Experiment Section

Materials. The steam treated USY500 (Si/Al = 325) and USY15 (Si/Al = 7.3) were obtained from TOSOH. The elemental analysis of the solid samples was performed using inductively coupled plasma (P-4010/ICP-AES). The total acid quantity of the USY500 and USY15 was calibrated to be 0.02 mmol/g and 0.21 mmol/g, respectively. All samples were calcined at 400^{o}C under vacuum 2 h before use.

2 Solid-state NMR

^{27}Al MAS NMR was used to distinguish the Al^{3+} species with different coordination numbers in USY. ^{27}Al MAS NMR spectrum was obtained on 400WB AVANCE III spectrometer, at the Larmor frequency of 104.34 MHz. The one pulse sequence was adopted, with a 10° pulse, a delay time of 0.4 s and a scanning number of 8000. The chemical shift was referenced to 1 M $AlCl_3$ aqueous solution. In addition, the acidic properties of solid state catalysts (USY) were characterized by using ^{31}P MAS NMR, based on the change of the P chemical shift after TMPO (trimethylphosphine oxide) adsorption. For the ^{31}P MAS NMR measurement, the sample was introduced into a glass tube, which was connected to a vacuum system. The pretreatment was carried on 400^{o}C for 2 h under vacuum (10^{-1} Pa). After adsorption TMPO at room temperature, the glass tube was isolated and transferred to a glove box. Under dry nitrogen, the sample was packed into a 4 mm ZrO_2 rotor and closed with Kel-F lids. All NMR experiments were performed on 400WB AVANCE III spectrometer at room temperature. ^{31}P MAS NMR spectra were obtained on 400WB AVANCE III spectrometer at the resonance frequency of 161.9 MHz, using 30° pulses with a recycle delay of 15 s at a MAS speed of 12 kHz. $NH_4H_2PO_4$ was used as a standard sample for chemical shift reference.

3 *S*ynchrotron XRD and Rietveld refinement of USY before and after pyridine adsorption.

High resolution Synchrotron XRD data were collected on Beamline I11, Diamond Light Source, UK. A detailed description of the beamline can be found elsewhere.[1] The energy of the incident X-ray beam was set at 15 keV. The wavelength and the 2θ-zero point correction were refined using a diffraction pattern obtained from a high quality silicon powder (SRM640c). For room temperature, the fine USY powder was loaded in a 0.5 mm borosilicate glass capillary, the physisorbed water in USY were desorbed under vacuum at 400 °C for 2 h. High resolution XRD data were obtained from the samples using the multi-analyser crystal (MAC) detectors. The patterns were collected in the 2θ range 0-150 ° with 0.001° data binning. Each pattern was collected for an hour for good statistics. In total, there were more than 500 *hkl* reflections measured, of which at least 100 independent *hkl* reflections were observed. In a crystallographic point of view, the number of structural variables should not exceed the number of *hkl* reflections in a refinement. In the Rietveld refinements, the number of structural parameters has not exceeded 100.

Using the TOPAS software, the diffraction patterns were analyzed by Rietveld refinement methods to obtain structural details. The starting coordinates were based on the Y zeolite model by Hriljac et al. for structural refinement.[2] The Thompson-Cox-Hastings pseudo-Voigt peak function[3] was applied to describe the diffraction peaks. The scale factor and lattice parameters were allowed to refine for all the diffraction patterns. The refined structural parameters for pattern were the fractional coordinates (x, y, z) and isotropic displacement factors (B_{eq}) for all USY atoms, and the site occupancy factors (SOF), translation and rotation axes for the rigid body Z-matrices describing the adsorbed pyridine molecules within the USY framework. The quality of the Rietveld refinements of synchrotron XRD data has been assured with a low goodness-of-fit (Gof) factor, a low weighted profile factor ($_{Rwp}$) and a well-fitted pattern with acceptable temperature factor (B_{eq}) within experimental errors. All the errors of the atom-atom distances were calculated from the square root of the $(X_{error})^2+(Y_{error})^2+(Z_{error})^2$ multiplied by the measure distances., The crystallographic data and refinement details are summarized in Table S1.

Table S1 Crystallographic data and details of the USY samples before and after pyridine-adsorbed

	USY500	USY15	Py·USY500	Py·USY15
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group	*Fd-3m*	*Fd-3m*	*Fd-3m*	*Fd-3m*
Py per unit cell	0	0	0.59	3.81
2θ range refinement (°)	3 – 55	3 – 55	3 - 55	3 – 55
Detector	Multi-analyser crystals			
Number of parameters	34	39	40	53
Number of hkls	563	563	563	563
Refinement	Rietveld	Rietveld	Rietveld	Rietveld
a (Å)	24.26653(4)	24.27051(3)	24.26613(4)	24.27194(3)
V (Å^3)	14289.705(74)	14296.742(52)	14288.991(72)	14299.250(47)
R_{wp} / $R_{p.}$ / $R_{exp.}$ (%)	8.916/6.879/3.474	9.561/7.205/2.616	9.718/7.469/2.942	8.790/6.938/2.595
Gof χ2	2.567	3.654	3.303	3.387
Wavelength (Å)	0.82593(2)	0.82593(2)	0.826209(3)	0.826209(3)
2 θ Zero point (°)	-0.00506(2)	-0.00506(2)	-0.000489(2)	-0.000489(2)

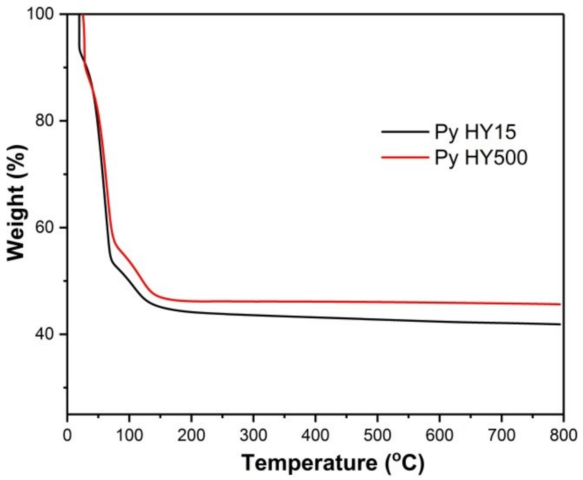


Figure S1 TGA data of USY15 and USY500 (ramp rate 10 °C min^{-1})

Refinement Procedure:

Since all samples were pre-treated at 400 °C under vacuum 2 h before use, the adsorbed water were removed completely (Figure S1). Accounting to the size of extra-framework Al^{3+} species, Al^{3+} and $Al(OH)^{2+}$ were used to fit the data in USY15, and the R_{wp} was found to be 9.561 and 14.540, respectively. This indicated one Al^{3+} ion in the sodalite cage of USY15 (if this one extra-framework Al^{3+} species was not added, the R_{wp} would turn to larger than 10).

The rigid body of Pyridine molecule was added into USY one by one (Py1, Py2, Py3,…). R factors were used to gauge the quality of refinement. With the progressive increase in the number of pyridine molecules, the R-factors were found decreasing, which indicates the use of a higher number of pyridine is approaching to the real structure in USY15. It was until the third pyridine, the R-factor was almost unchanged. However, the pseudo 'third' pyridine appeared at the position very close to Py2 (within 0.9 Å) which shared the site occupancy of Py2. Thus, we excluded the Py3 to be a genuine position, which was possibly arisen owing to the distortion/displacement of Py2 thermal motion, etc. As a result, 2 pyridine molecules were used to fit all the synchrotron PXRD data accordingly.

In USY500, the rigid body of Pyridine molecule was added into USY500 one by one (Py1, Py2,…). R factors were used to gauge the quality of refinement. With the progressive increase in the number of pyridine molecules, the R-factors were found decreasing, which indicates the higher number of pyridine was deviating from the real structure in USY500. With the progressive increase in the number of pyridine molecules to 2, the occupancy of the Py2 was also decreased to zero. As a result, 1 pyridine molecule was used to fit all the synchrotron PXRD data accordingly.

3.1 The Fourier maps of Al sites and pyridine sites in USY

A Fourier map was generated between the observed and calculated scattering data over the 2θ range of 3 – 55°. It was used to identify the positions with the highest remaining electron density in the framework, which can indicate the possible positions of the inorganic or organic small molecules (Fig. S2).

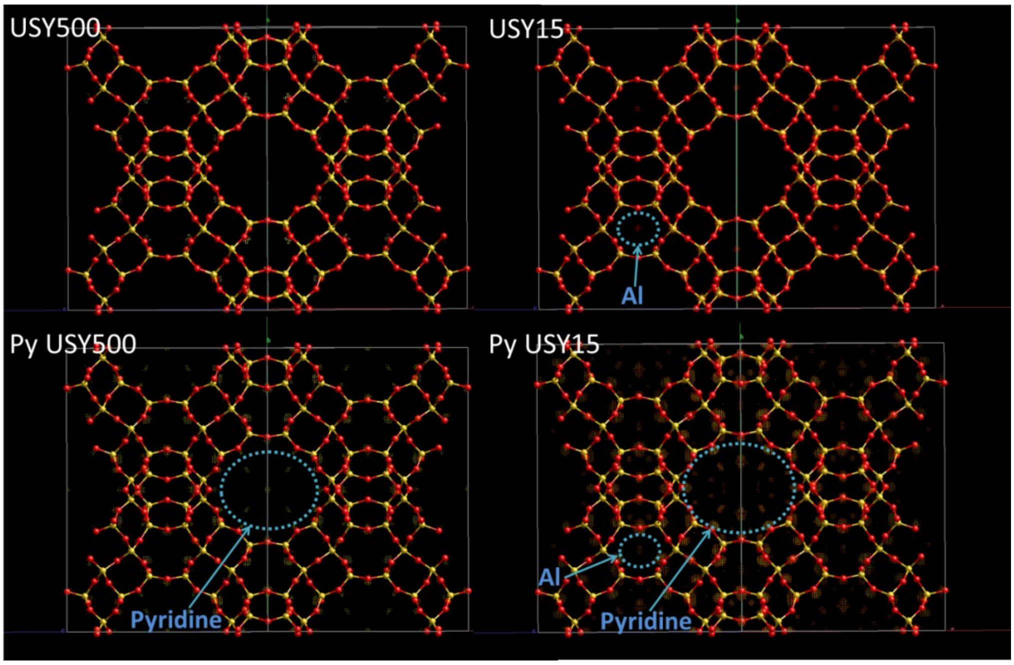


Figure S2. Fourier maps of USY500, USY15 and pyridine molecules pre-adsorbed on USY500 and USY15 at room temperature; the blue circles represent the possible electron densities and positions of Al and pyridine.

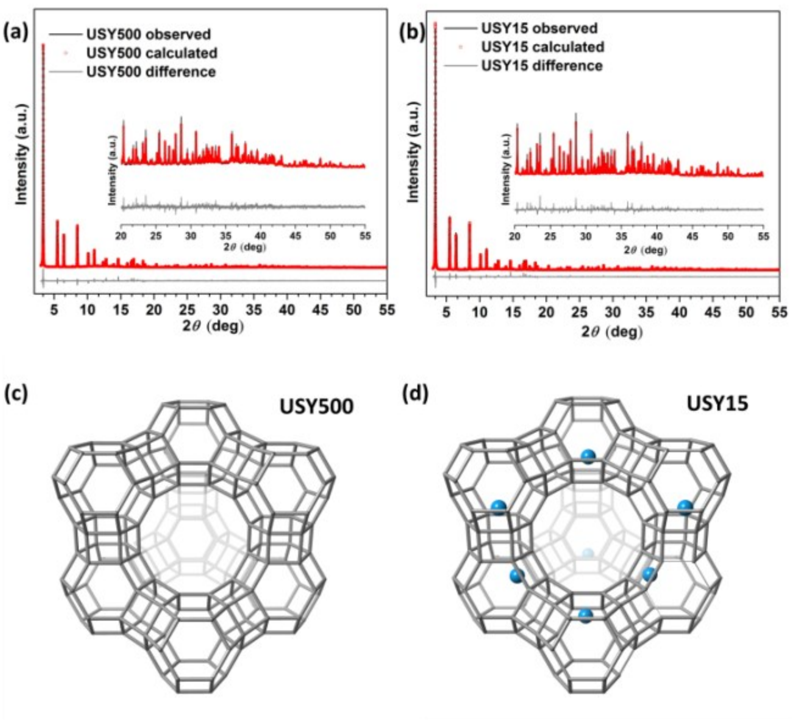


Figure S3. SXRD patterns and Rietveld refinement data of (a) USY500 and (b) USY15. The zooms highlight the 20 – 55^o 2θ range to illustrate the quality of the refinement. The structure of (c) USY500 and (d) USY15 with stick model without symmetrically appearing 4-CN extra-framework Al^{3+}. Grey represents the USY; Blue represents Al (4-CN extra-framework Al^{3+} species).

Synchrotron X-ray powder diffraction (SXRD) was employed in this work. The SXRD patterns of USY500 (Fig. S3a) and USY15 (Fig. S3b) were refined by the Rietveld method using TOPAS software (Bruker AXS, version 5). Both refinements started from the zeolite Y (purely siliceous) crystal structure.[2] The negligible electron scattering density inside the cage after the high temperature and vacuum pretreatment enabled an accurate optimization of the atoms of the framework. The acceptable R-factors, R_{wp} 8.916% and 9.561% clearly showed the high quality of the refinement. In Fig. S2c, no extra-framework Al^{3+} species exists in USY500, consistent with the ^{27}Al NMR result. On the contrary, extra-framework Al^{3+} can be clearly refined in sodalite cages of USY15 with 2.17(11) Al^{3+} per unit cell (Table S3). To balance the charge of the USY15 when those Al^{3+} exist, some proton obtained from the 4-CN framework Al^{3+} will be lost. So, the detectable numbers of the BAS will be less than the numbers of the 4-CN framework Al^{3+}. Rietveld refinement has also been applied to locate the adsorbed pyridine molecules with respect to the positions of the BAS. Their inter-atomic distances may reflect the nature and strength of the acid site adducts (Table S4).[4]

3.2 The Rietveld refinement and details of pyridine-free and pyridine-adsorbed USY at room temperature.

After some preliminary B_{eq} refining, the observed trend of non-framework atoms B_{eq} affected on R factors is small. Therefore, the non-framework atoms B_{eq} were fixed at $B_{eq}(N) = 5$, $B_{eq}(C) = 7.5$ and $B_{eq}(Al) = 5$. In addition, an amorphous peak at 3.18° to 3.22° had been added during all the refinement. Then atom number per unit cell was calculated from SOF × symmetry multiplicity.

Table S2. Crystallographic information files from the Rietveld refinement of USY500

Species	Atom	X	y	z	SOF	B_{eq} (Å^2)	Symmetry multiplicity/ Wyckoff
Zeolite framework	Si1	-0.05445	0.12551	0.03467	1	0.909(14)	192i
	O1	0	0.89629	0.10371	1	0.967(27)	96h
	O2	-0.00766	-0.00766	0.14149	1	0.967(27)	96g
	O3	0.07811	0.07811	-0.03595	1	0.967(27)	96g
	O4	0.07193	0.07193	0.31444	1	0.967(27)	96g

All the T-sites (T=Al, Si) of USY500 refined using the same B_{eq} parameter.
All the O-sites of USY500 share the same B_{eq} parameter.

Table S3. Crystallographic information files from the Rietveld refinement of USY15

Species	Atom	X	y	Z	SOF	B_{eq} (Å^2)	Symmetry multiplicity /Wyckoff
Zeolite framework	Si1	-0.05409	0.12560	0.03495	1	0.765(11)	192i
	O1	0	0.89589	0.10411	1	0.737(18)	96h
	O2	-0.00739	-0.00739	0.13986	1	0.737(18)	96g
	O3	0.07919	0.07919	-0.03568	1	0.737(18)	96g
	O4	0.07140	0.07140	0.31774	1	0.737(18)	96g
Extra-framework Al	Al	1.365(3)	-0.142(2)	0.255(4)	0.0113(6)	5.0(17)	192i

All the T-sites (T=Al, Si) of USY500 refined using the same B_{eq} parameter.
All the O-sites of USY500 share the same B_{eq} parameter.

Table S4. Crystallographic information files from the Rietveld refinement of Py·USY500

Species	Atom	X	Y	Z	SOF	B_{eq} (Å^2)	Symmetry multiplicity /Wyckoff
Zeolite framework	Si1	-0.05445	0.12551	0.03467	1	0.685(15)	192i
	O1	0	0.89629	0.10371	1	1.152(25)	96h
	O2	-0.00766	-0.00766	0.14149	1	1.152(25)	96g
	O3	0.07811	0.07811	-0.03595	1	1.152(25)	96g
	O4	0.07193	0.07193	0.31444	1	1.152(25)	96g
Py1	translate	0.248(1)	0.251(2)	0.403(3)			
	N	0.248	0.251	0.403	0.0371(4)	5	16
	C1	0.301	0.233	0.401	0.0371(4)	7.5	16
	C2	0.333	0.224	0.447	0.0371(4)	7.5	16
	C3	0.311	0.236	0.499	0.0371(4)	7.5	16
	C4	0.228	0.262	0.453	0.0371(4)	7.5	16
	C5	0.319	0.224	0.360	0.0371(4)	7.5	16

All the T-sites (T=Al, Si) of USY500 refined using the same B_{eq} parameter.
All the O-sites of USY500 share the same B_{eq} parameter.
All the C-sites and N-sites of pyridine refined using the fixed B_{eq} 5 and 7.5, respectively.

Table S5. Crystallographic information files from the Rietveld refinement of Py·USY15

Species	Atom	*X*	*Y*	*Z*	SOF	B_{eq} (Å^2)	Symmetry multiplicity /Wyckoff
Zeolite framework	Si1	-0.05409	0.12560	0.03495	1	0.766(10)	192i
	O1	0	0.89589	0.10411	1	0.737(18)	96h
	O2	-0.00739	-0.00739	0.13986	1	0.737(18)	96g
	O3	0.07919	0.07919	-0.03568	1	0.737(18)	96g
	O4	0.07140	0.07140	0.31774	1	0.737(18)	96g
Extra-framework Al	Al	1.365(3)	-0.142(2)	0.255(4)	0.0113(6)	20(4)	192i
Py1	translate	0.249(1)	0.252(2)	0.403(3)			
	N	0.249	0.252	0.403	0.1056(46)	5	16
	C1	0.288	0.244	0.442	0.1056(46)	7.5	16
	C2	0.279	0.251	0.498	0.1056(46)	7.5	16
	C3	0.2227	0.266	0.515	0.1056(46)	7.5	16
	C4	0.185	0.274	0.476	0.1056(46)	7.5	16
	C5	0.198	0.266	0.421	0.1056(46)	7.5	16
Py2	translate	0.119(3)	1.902(4)	-0.371(4)			
	N	0.119	1.902	-0.371	0.1327(26)	5	16
	C1	0.122	1.878	-0.422	0.1327(26)	7.5	16
	C2	0.122	1.906	-0.471	0.1327(26)	7.5	16
	C3	0.118	1.964	-0.469	0.1327(26)	7.5	16
	C4	0.115	1.990	-0.418	0.1327(26)	7.5	16
	C5	0.116	1.958	-0.371	0.1327(26)	7.5	16

All the T-sites (T=Al, Si) of USY500 refined using the same B_{eq} parameter.

All the O-sites of USY500 share the same B_{eq} parameter.

All the C-sites and N-sites of pyridine refined using the fixed B_{eq} 5 and 7.5, respectively.

4 Diels–Alder reaction

4.1 Potassium exchanged USY15 samples:

The potassium partial or total exchanged USY15 zeolites (low K/USY15 and high K/USY15) were prepared by impregnating 1.0 g of the commercial USY15 zeolite with 1 mL solution of KNO_3 (low K/USY15: 0.18 mol.L^{-1}; high K/USY15: 0.62 mol.L^{-1}). The samples were dried overnight at 100°C and then calcined at 450°C for 3h.

As seen from Fig. 2 in the main manuscript, the refined structure of pyridine-adsorbed USY15 shows an additional distorted 4-CN extra-framework Al^{3+} site in a sodalite cage that is normally unoccupied. There are also two distinctive pyridine sites in the supercage with the distances of N_{Py1}-O4 and N_{Py2}-O4 are 2.73(1) Å and 3.21(2) Å, respectively. The Py2 with the longer N_{Py2}-O4 3.21(2) Å distance, which is structurally linked to the extra-framework Al^{3+} through the first coordinated O4 at the interface between sodalite and supercage, indicating the enhanced acidic strength of the BAS O4. The amount of the stronger BAS was found to be 2.13(1) S-BAS/unit cell. Combined with the NMR result of the W-BAS: S-BAS = 2.4: 1, the amount of the W-BAS was calculated to 5.11.

4.2 Reaction conditions:

In a typical experiment, 15 mL of the model compound 2,5-Dimethylfuran (99% Sigma-Aldrich), 8.2 mL of ethanol (99.5% Sigma-Aldrich) and 0.4 g of zeolite were used over a temperature range of 200 to 300 °C and 1.0 mL of tridecane as an internal standard. The reaction vessel was flushed with inert gas (N_2). Liquid products were identified and quantified using a gas chromatograph/mass spectrometer (Agilent 6890 and Agilent MSD 5973 (N)) calibrated with pure standards. After reaction, the autoclave was cooled down to −60°C by dry ice/acetone bath. The gas products (CO, CO_2, CH_4) analyzed by a Perkin Elmer Autosystem XL Arnel Gas phase GC-FID-Methanator. C_2H_4 gas product was assumed to be mainly produced from ethanol. The solid residue was filtrated and washed with acetone and dried overnight (80 °C). Then it was analyzed by thermogravimetric analyses (TA instruments Q50), the samples were heated at 10 °C min^{-1} from room temperature to 900 °C under air to quantify the coke on zeolite to complete the carbon balance. The conversion was expressed in term of the molar conversion of 2,5-dimethylfuran and carbon balance was achieved at the minimum of 90-95%.

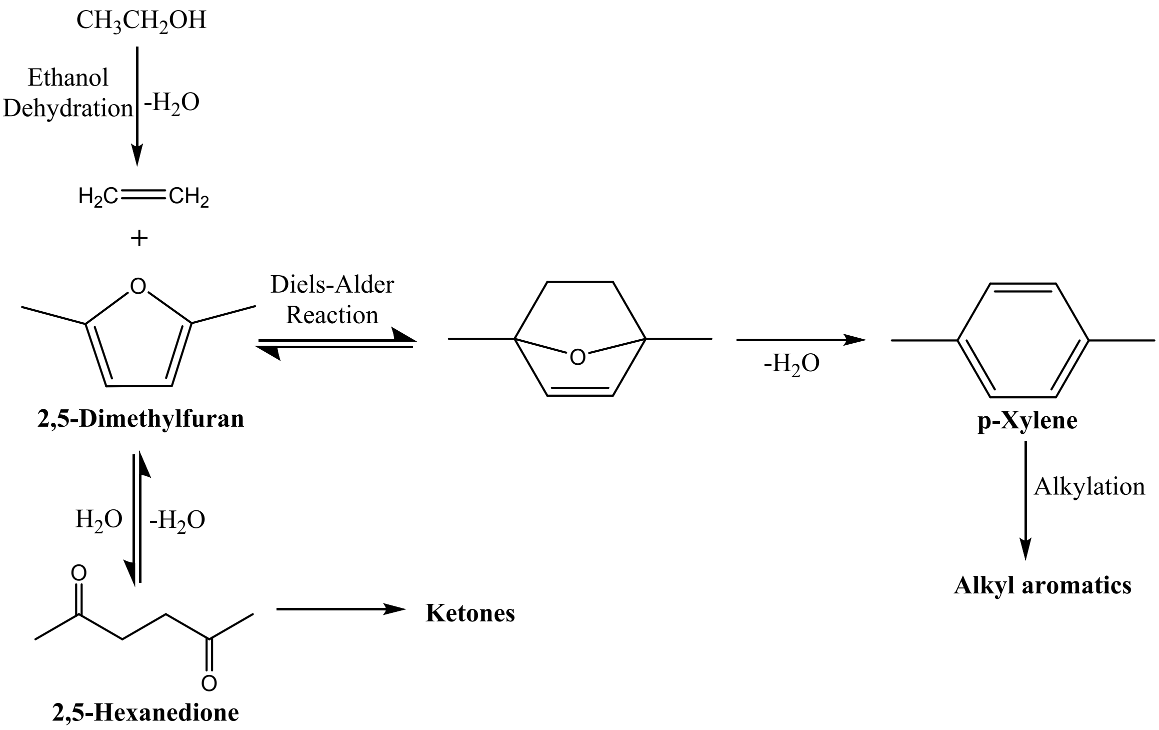


Figure S4. Schematic representation of the conversion of 2,5-dimethylfuran (DMF) into aromatics by Diels-Alder cycloaddition with ethylene, *in-situ* generated by dehydration of ethanol, and the DMF hydrolysis equilibria forming 2,5-hexanedione.

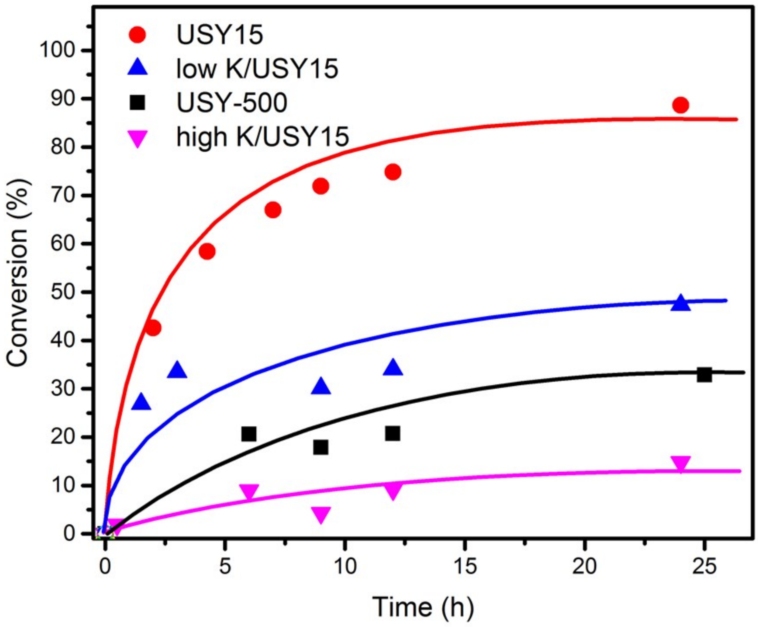


Figure S5. Kinetic data derived for 0.14 mole DMF transformation over 0.4 g catalyst with ethylene generated *in situ* from ethanol (0.14 mole) in 50mL at 250°C.

5 *S*ynchrotron XRD and Rietveld refinement of USY after potassium loading.

Potassium partial or total exchanged USY15 zeolites (low K/USY15 and high K/USY15) were prepared by the impregnation method, 2.13 K^+/unit cell were put into the low K/USY15 sample to specifically block the strong BAS, 7.24 K^+/unit cell were put into the high K/USY15 to block all the BAS.

The SXRD patterns of K^+ ion-exchanged low K/USY15 (Fig. S6a) and high K/USY15 (Fig. S7a) and inserted zoom in 20 – 55^o 2θ range data and the acceptable Rwp of 9.631% and 8.053% illustrate the high quality of the refinement (Tables S7-S9). During the K^+ ion-exchanged USY15 refinement, the previous extra-framework Al^{3+} positions in sodalite cage were fixed.

The refined structure of the low K/USY15 shows only one K^+ site (K1) located in supercage which indeed interacts only with the strong BAS O4 with ultra-selectivity, giving the distance of 3.57(1) Å (Fig. S6b). The amount of the K1 is 2.04(5) K^+/unit cell, which indicates 96% of the deposited K^+ (2.13 K^+/unit cell) exchanges with the strong BAS protons during the ion-exchange step.

The refined structure of the high K/USY15 shows two K^+ sites, which relates to the K1/strong BAS O4 (the electron cloud of O is strongly polarized) interaction with the longer distance of 3.57(1) Å and K2/weak BAS O4 (the electron cloud of O is less polarized) interaction with the shorter distance of 3.22(2) Å, respectively (Fig.S7b). Depending on the sodalite cage occupancy with or without extra framework Al^{3+}, different K-O4 distances again demonstrate the different acidic strengths of the O4 sites. The amounts of the K1 and K2 in the high K/USY15 is found to be 2.33(4) K^+/unit cell and 5.10(4) K^+/unit cell, which are consistent with the previous pyridine-adsorbed SXRD and NMR results. In short, the USY-15 samples with specific blockage of strong BAS and total blockage of all BAS have been synthesized successfully. The detailed acid site distributions are listed in Table S6.

Table S6. Strong and weak Brønsted acid sites per unit cell, obtained by SXRD diffraction patterns and Rietveld refinement data after pyridine adsorption

Zeolite	Strong BAS	Weak BAS
USY15	2.13	5.11
USY500	-	0.60
Low K/USY15	-	5.11
High K/USY15	-	Trace

Table S7 Crystallographic data and details of the USY samples potassium loading

	Low K/USY15	High K/USY15
Crystal system	Cubic	Cubic
Space group	*Fd-3m*	*Fd-3m*
K^+ per unit cell	0	0
2θ range refinement (^{o})	3 – 60	3 - 60
Detector	Multi-analyser crystals	
Number of parameters	43	47
Number of hkls	702	702
Refinement	Rietveld	Rietveld
a (Å)	24.27348(4)	24.26952(4)
V (Å^3)	14301.978(68)	14294.984(74)
R_{wp} / $R_{p.}$ / $R_{exp.}$ (%)	9.631/7.098/3.201	8.053/5.056/3.056
Gof $\chi2$	3.001	2.635
Wavelength (Å)	0.82601(2)	0.82602(1)
2 θ Zero point (°)	0.01136(1)	0.01099(2)

5.1 low K/USY15 (block the strong BAS)

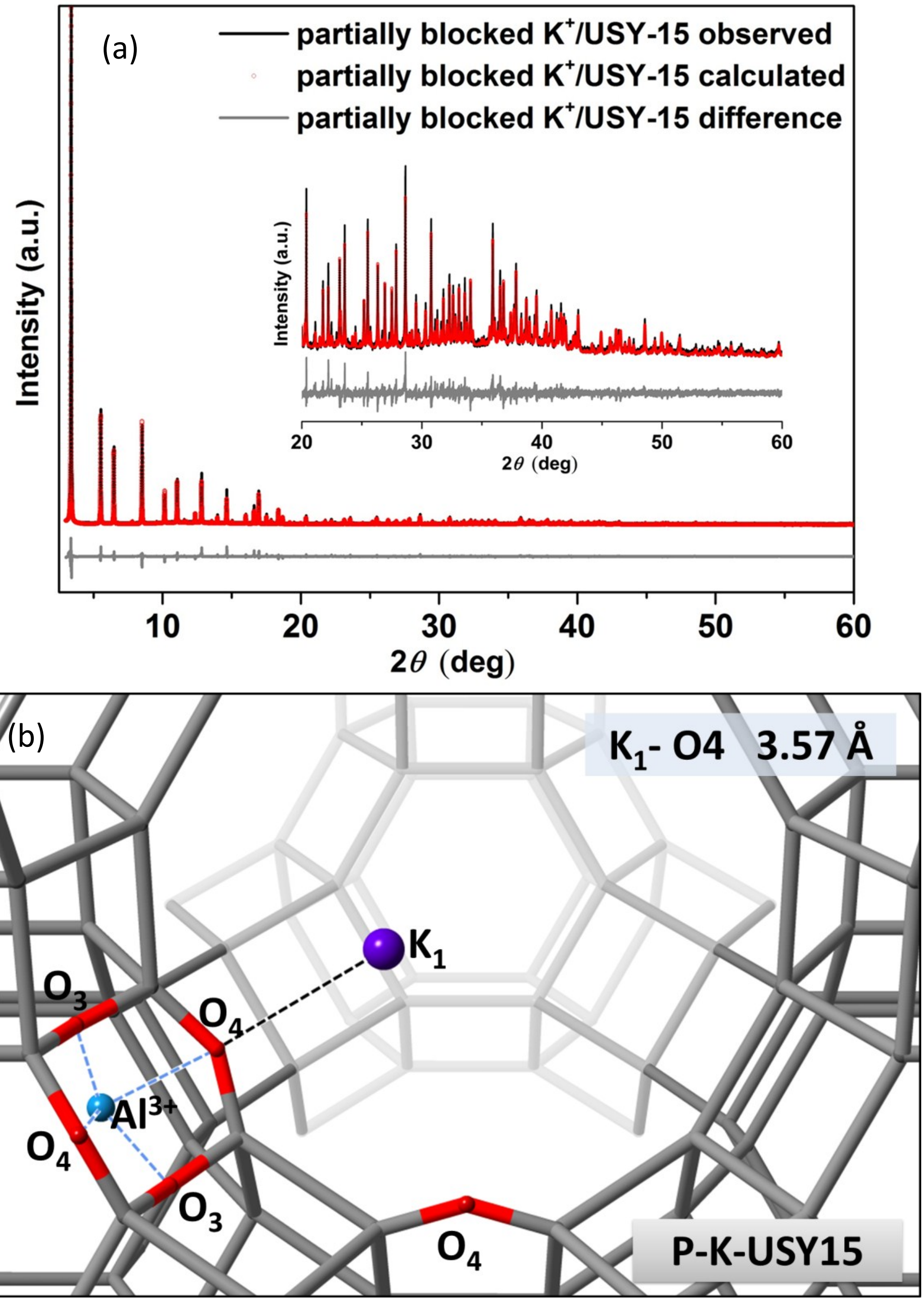
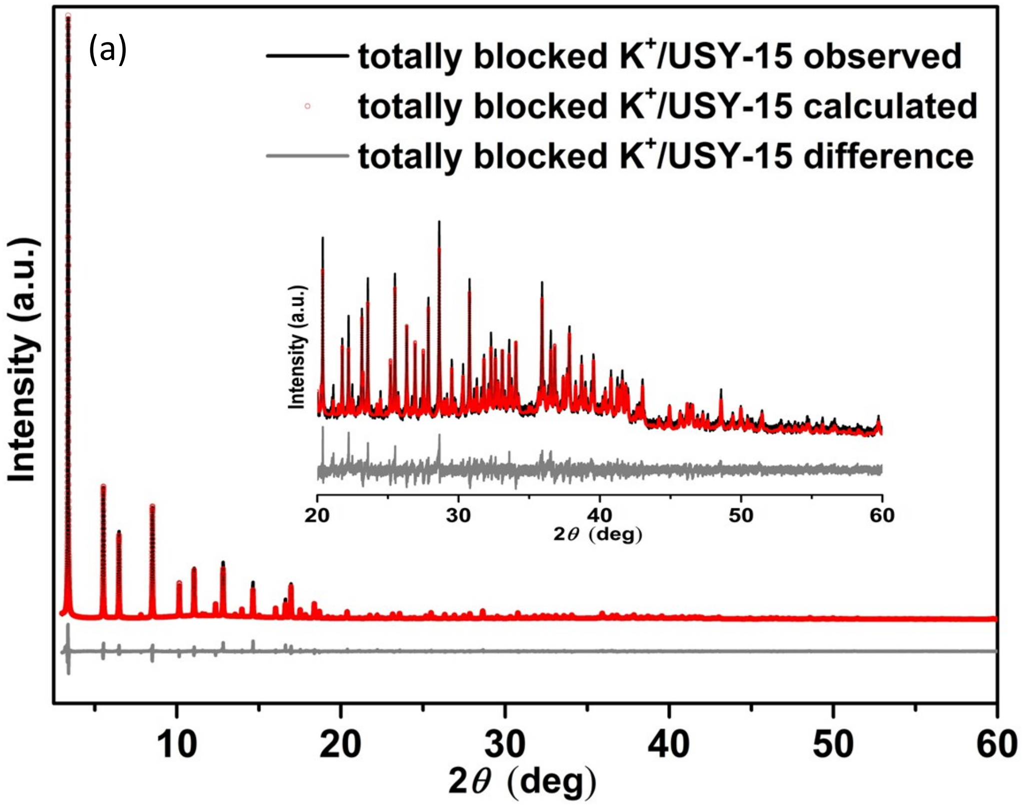


Figure S6. (a) top figure: the SXRD data of low K/USY15, fitted by using Rietveld refinement method. The data in the 2θ range of 20–60° is zoomed in to illustrate the quality of the refinement result; (b) bottom figure: refined structure of low K/USY15

Table S8. The atomic arrangement of low K/USY15

Species	Atom	X	Y	Z	SOF	B$_{eq}$ (Å^2)	Multiplicity
Zeolite framework	Si1	-0.0539	0.1258	0.0355	1	0.696(43)	192i
	O1	0	0.8958	0.1041	1	0.801(74)	96h
	O2	-0.0073	-0.0073	0.1398	1	0.801(74)	96g
	O3	0.0791	0.0791	-0.0356	1	0.801(74)	96g
	O4	0.0714	0.0714	0.3177	1	0.801(74)	96g
Extra-framework Al	Al^{3+}	1.365(3)	-0.142(2)	0.255(4)	0.0113(6)	19(7)	192i
K$^+$	K1	-0.016(2)	0.766(2)	1.354(1)	0.0213(5)	9(1)	96g

5.2 high K/USY15 (block the strong and weak BAS)



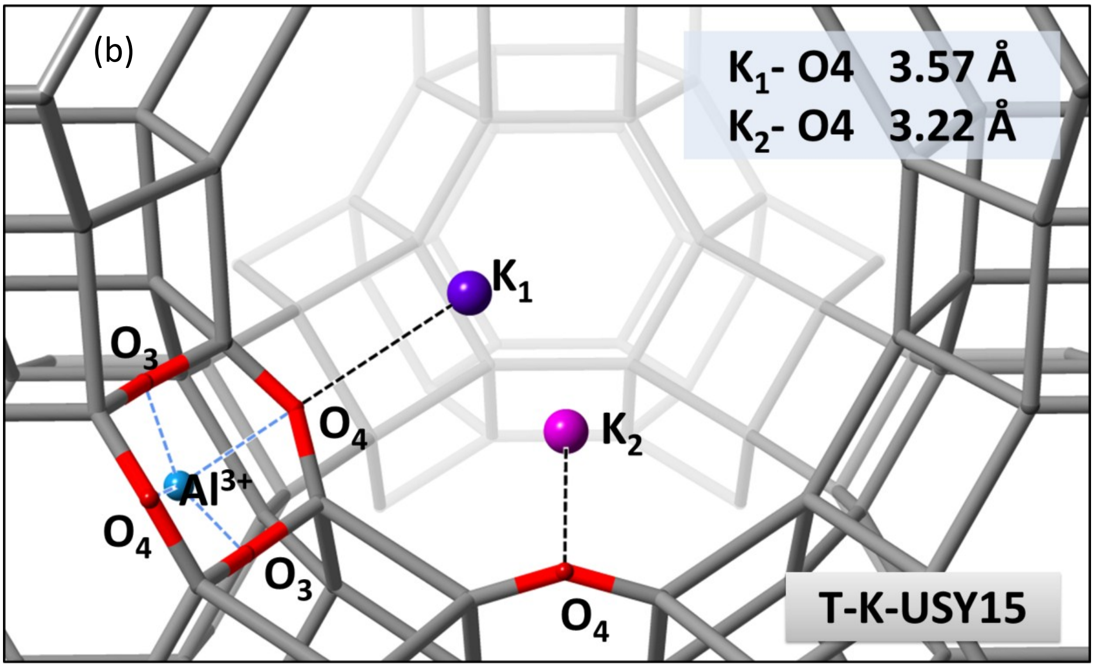


Figure S7. (a) top figure: The SXRD data of high K/USY15, fitted by using Rietveld refinement method. The data in the 2θ range of 20–60° is zoomed in to illustrate the quality of the refinement result; (b) bottom figure: refined structure of high K/USY15.

Table S9. The atomic arrangement of high K/USY15

Species	Atom	*X*	*y*	*Z*	SOF	B_{eq} (Å^2)	Multiplicity
Zeolite framework	Si1	-0.0536	0.1259	0.0354	1	0.826(14)	192i
	O1	0	0.8958	0.1041	1	0.968(30)	96h
	O2	-0.0073	-0.0073	0.1398	1	0.968(30)	96g
	O3	0.0791	0.0791	-0.0356	1	0.968(30)	96g
	O4	0.0714	0.0714	0.3177	1	0.968(30)	96g
Extra-framework Al	Al^{3+}	1.365(3)	-0.142(2)	0.255(4)	0.0113(6)	19(7)	192i
K+	K1	-0.011(1)	0.769(2)	1.351(1)	0.0243(4)	6.2(7)	96g
	K2	-0.101(4)	0.694(1)	1.347(4)	0.0531(4)	8.4(8)	96g

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