Elucidation of Molecular Adsorbate Structure on Brønsted Acid Site in microporous H-ZSM-5**

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Abstract: Microporous H-ZSM-5 containing one Brønsted acid site per asymmetric unit is deliberately chosen to host pyridine as guest molecules. By using in situ synchrotron X-ray powder diffraction combined with Rietveld refinement, the slight but significant alteration in scattering parameters of modified framework atoms by the adsorbed pyridine molecules enables, for the first time, to elucidate their adsorption geometries and interactions with the Brønsted acid site in H-ZSM-5 in terms of atomic distances and angles within experimental errors. This conclusion, although preliminary demonstrated in this specific H-ZSM-5 zeolite, would be expected to be transferable to other zeolites. It is believed that this technique can offer a stepping stone to lead to rational engineering molecular interaction(s) with acid site in zeolitic catalysis.

Petrochemical products have played an inarguably key role in the activity of mankind since the turn of the last century. The conversions of organics such as crude gas and oil into olefins and aromatics are very important catalytic reactions, as these constitute key platform chemicals in the synthesis of numerous commodity chemicals and polymer materials. Zeolites are one of the most commonly used catalysts for these conversions[1,2]. The recently expanded uses of zeolites in the conversion of biomass to petrochemical products and environmental applications are also of great significance[3]. As a class of aluminosilicate compounds (aluminium-doped silica) zeolites with doped Al generates charge imbalances within the microporous silica framework. In typical behaviour, H^+ moves close to the substituted Al atom to form a Brønsted acid site in zeolites; in principle this H^+ can be populated on either one of the four oxygen atoms bonded to each framework Al site, as demonstrated in the early work by Haag et al[4]. This protonic site can take up organic molecules and facilitate many acid-catalyzed hydrocarbon reactions, including isomerization, oligomerization, alkylation, and cracking, to name but a few examples[5,6]. Due to the combination of the intrinsic shape and size selectivity of internal channels and pore mouths[7] and mass

transport effects[8], zeolites can thus be used as versatile molecular sieves in selective molecular adsorption and catalysis reactions. This also represents single-site in a confined spatial environment in heterogeneous catalysis and could provide understanding of homogeneous molecular approach to heterogeneous catalysis. The site is well defined and periodically distributed with a definite chemical surrounding, as in conventional homogeneous systems, but shows all the advantages of heterogeneous systems, in terms of easy separation, recoverability and recyclability. Despite the extensive applications of zeolites and the importance of obtaining mechanistic information[5,6], the nature of interaction between organic adsorbate and Brønsted acid site is in fact not well understood. This is largely due to the fact that most spectroscopic methods (IR, Raman, NMR) and thermal methods (TPD, TGA) have limitations in providing structural information of molecular adsorbate in the local atomic arrangement with respect to framework atoms[1,2,9–12]. There have been some recent significant achievements in modelling of zeolites (e.g. DFT, QM/MM, ONIOM) to describe acid sites and adsorbed molecular species in the region of interest (i.e. reactant on catalytic acid site) at quantum mechanical level, whereas the framework atoms are treated by classical force field equations[12–17]. Besides, it is becoming clear that the Al location and distribution in the zeolite framework are not random or controlled by simple theoretical rules[18,19]. They depend on the conditions of the zeolite synthesis and the fundamental spatial interaction(s) between molecular adsorbate and protonic or transition metal ion-containing zeolites can critically affect adsorption, separation and catalytic activity/selectivity. In addition, the number of new zeolite structures for potential energy saving catalytic processes, environmentally benign sorbents, storage materials for waste and energy, etc. has been rapidly growing since the past decade[20,21]. Thus, a reliable experimental method is needed to reveal the atomic arrangement of adsorbate with reference to acid site to guide a rational design of zeolites in catalysis.

Recently, the advancement of diffraction facilities using high resolution synchrotrons has provided chemists a powerful tool in studying porous but periodic materials. For example, synchrotron X-ray powder diffraction (SXPD) data was used to determine the structure of various zeolites[22–24], also the positions of Na^+ and K^+, and Cs^+ ions in zeolite A and H-ZSM-5[25,26]. The determination of carbon dioxide and sulfur dioxide adsorbate structures in metal-organic frameworks (MOF) by SXPD, and the determination of water molecules in zeolite-related materials (SAPO) by neutron diffraction, have recently been established[27,28]. In this study, H-ZSM-5 containing one Brønsted acid site per asymmetric unit in the framework is deliberately chosen as a model solid Brønsted acid. By taking advantages of the molecular specificity of pyridine molecule (C_5H_5N) as a chemical probe to the protonic acid site of H-ZSM-5 by forming acid-base adducts and the slight but significant alteration in scattering parameters of the underneath adsorbent

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atoms in close proximity, their interactions with the Brønsted acid site in H-ZSM-5 using SXPD at an atomistic level within experimental error is revealed. The Rietveld refinements of these high resolution SXPD data clearly suggest that a pyridinium ion is first formed with the strong primary Brønsted protonic acid site (Al-O(H)-Si) upon adsorption of pyridine, which then acts as a weaker secondary Brønsted acid site to interact with another pyridine molecule to form a 'dimer' like species through H-bonding (see Fig. S3). By the comparative study of less sterically crowded ammonia (NH_3) as a probe, related adsorption structures with the Brønsted acid site within the confined cavity of H-ZSM-5 can also be obtained (see Fig. S4). Accordingly, the intrinsic acidity is not only the parameter to reflect catalytic performance for acid-catalyzed reactions, but the geometry for adsorption and stabilization of the activated H^+-guest complex with respect to other adsorbate(s) in zeolite should also be considered[17]. Like enzyme systems, the tertiary structure with substrate molecule(s) will determine the spatial conformation as well as the number of hydrogen bonds of the 'protonated complex' with the framework anion in order to get stereo-specificity.

H-ZSM-5, a commercial sample, was supplied by SRIFT-Sinopec, China. According to ICP-AES and ^{27}Al NMR characterization (see Fig. S1), the structural formula of this H-ZSM-5 is written as $H_{4.48}Al_{4.48}Si_{91.52}O_{192}$. This predominantly corresponds to about one Al at one specific site per asymmetric unit (called 'as-unit' in this paper) (With the space group of Pnma (see Table S1), the H-ZSM-5 contains four as-units which possess a mirror plane in between.) in the framework as suggested by the highly symmetric peak in ^{27}Al NMR[28]. TEM and SEM images show that this H-ZSM-5 has a uniform morphology (see Fig. S5). As measured by BET isotherm, the diameters of the H-ZSM-5 particles are around 2 µm with surface area of 330 m^2 g^{-1} and the calculated micropore volume is 0.179 cm^3 g^{-1} which falls in range of an expected MFI ZSM-5 structure. HRTEM lattice pattern also shows the highly crystalline framework of H-ZSM-5. The crystallographic fringe distance is 1.11 nm, corresponding to the d spacing of the (101) phase in H-ZSM-5 (see Fig. S5(d)). This low acid site value was deliberately used due to the well-dispersed of Brønsted acid sites in the framework, hence facilitating the study of steric interactions with adsorbate(s). First, the H-ZSM-5 sample was pre-saturated with pyridine vapor before it was ramped gradually in thermogravimetric analysis equipment (TGA) in a flowing stream of air (60 cm^3 min^{-1}). As observed from the differential thermogravimetric curve (DTG) (see Fig. S6(a), the desorption processes of pyridine are likely under a diffusion controlled regime with typical low desorption temperatures below 380 °C. There are two distinct desorption profiles, which indicate the existence of two distinctive interactions between pyridine molecules with the host zeolite. One pyridine desorbs at lower temperature, while the other at higher temperature, giving a roughly 1:2 molecular ratio. The apparent activation energies (E_a) for the two pyridine desorption profiles have been calculated using Arrhenius plots derived from the TGA traces (see Fig. S6), which correspond to 24.93 ± 0.03 kJ mol^{-1} and 39.85 ± 0.04 kJ mol^{-1} (see Fig. S7). These low values indeed reflect the typical diffusion limitations due to the microporosity of the zeolite. From calibration, the total number of desorbed pyridine molecule

from TGA is about 5.32 per unit cell of dried H-ZSM-5 from room temperature to 600 °C with no evidence of further desorption of pyridine beyond this temperature due to levelling of the thermal baseline. This corresponds to 1.33 pyridine molecules per one Brønsted acid site per as-unit. Therefore, this implies the co-existence of one pyridine monomer and dimer per acid site. It is well known that the Brønsted acid site in H-ZSM-5 with extremely strong acidity can protonate organic adsorbates[6]. Thus, the strongly bounded pyridine molecule as a monomer (PyrH$^+$) is expected to be thermally more stable than those of the dimer ([PyrH···Pyr]$^+$) where the second pyridine molecule is likely held by the primary protonated pyridinium ion through a weaker hydrogen bonding interaction. According to the peak fit of the DTG data, the sample contains 0.88 strongly bounded PyrH$^+$ (in both the monomer and dimer) and 0.44 weakly bounded Pyr (second Pyr in dimer) per acid site in 1:2 ratio, as revealed by the thermogravimetric analysis. Similarly, a FTIR peak at 1540 cm^{-1} attributed to PyrH$^+$ and a broader peak at 1450 cm^{-1} of weaker proton interaction with pyridine can also be seen from Fig. S8 in SI. Solid state NMR spectroscopy was used to qualitatively differentiate adsorption structures in this zeolite. From the NMR spectrum (see Fig. S2) two peaks, one at -92.8 ppm (broad peak) and one at -176.0 ppm (sharper peak), can indeed be identified. The former broad peak is attributed to ^{15}N-pyridine molecules with a long range coupling with H$^+$ in the [PyrH···Pyr]$^+$ dimer and the latter sharp peak matches with the typical literature peak value of pyridinium ion (PyrH$^+$) with stronger ^1H-^{15}N coupling for the greater downshift in chemical shift of ^{15}N of pyridine[29].
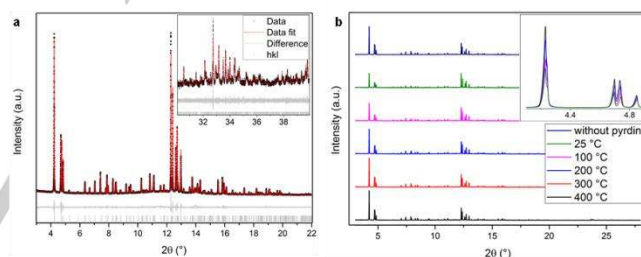

Figure 1. (a) Rietveld refinement of H-ZSM-5 pre-saturated with pyridine at 100 °C, and (b) high resolution SXPD patterns of unloaded H-ZSM-5 samples and pyridine adsorbed samples at various desorption temperatures. The crystal structures of H-ZSM-5 zeolite (as shown in Fig. S3) and adsorbed pyridine molecules were determined using Rietveld refinement method. Upon adsorption of pyridine, the parent structure of the H-ZSM-5 zeolite is not altered with the lattice parameters maintained (see Table S1). However, the increase in intensity at low 2θ peaks indicates desorption of pyridine in the host zeolite. The atomic parameters of the SXPD data at 100 °C are summarized in Tables S2 and S3. From these atomic coordinates, a crystal model was constructed and is displayed in Fig. 2

Thus, according to the above NMR, TGA and FTIR (see Fig. S2, S6-S7), there are two fundamental interactions of pyridine molecules with the H-ZSM-5 framework. Under our preparation conditions, there is a co-existence of pyridine monomer and dimer forms within the zeolite. However, their atomic positions with respect to the Brønsted acid site of this zeolite are not known. Synchrotron X-ray powder diffraction (SXPD) can give statistical average atomic positions of the isomers with respect to this H-ZSM-5 containing one defined Brønsted acid site in each as-unit, Rietveld refinement was therefore used to elucidate their structural details. To model a dimeric interaction, two separate Z-matrices were used to place two pyridine

molecules into the H-ZSM-5 framework containing one Brønsted acid site in each as-unit (see Fig. 1(a)).

Figure 2 and Table S2 show the atomic coordinates derived from Rietveld refinement at 100 °C (these data are particularly used for comparison due to the reduced extent of water physisorption at this temperature), where N1 and N2 denote the nitrogen atoms of pyridine 1 (Pyr1) and pyridine 2 (Pyr2) molecules within the zeolitic framework. Although the uncertainty errors in atomic positions of adsorbed pyridine molecules are higher than that of rigid structural elements (O, Si) due to intrinsic higher degrees of freedom and higher isotropic temperature factor, Beq, (see Table S2), the generally low but acceptable Rwp and χ^2 values with a closely fitted pattern suggest a good quality of refinement indicating the reliability of the atomic positions and angles within experimental errors. As seen in Methods (SI), 4190 hkl reflections (more than 300 independent hkl reflections) have been used for the calculations, which allow a great number of structural variables (less than 160 in the refinements) to be refined in a satisfactory manner.
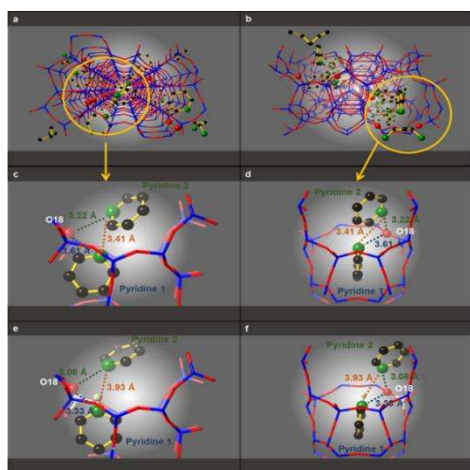

Figure 2. (a) – (b) Crystal structures obtained from the Rietveld refinement for pyridine pre-adsorbed H-ZSM-5 at 100 °C: (a) the unit cell from [100] direction (straight channel view), showing two pyridine sites, the others are symmetry related to these, (b) the unit cell from [010] direction (sinusoidal channel view), (c) a zoom-in (straight channel view), showing the locations of the nitrogen and oxygen atoms in the framework, and (d) another zoom-in (sinusoidal channel view). (e) – (f). Force field optimized model of pyridine adsorbed H-ZSM-5 with Pyr1 taken a proton to form pyridinium ion, viewed in the same direction as for (c, d). Atoms are represented as: blue sticks = Si/Al, red sticks/balls = O, green balls = N, black balls = C.

From the derived Refinement data presented in the Fig. 2 and Table S2, it is interesting to reveal that Pyr1 and Pyr2 molecules are both located in the cross-channel region, Pyr1 is near the sinusoidal channel while Pyr2 is near the straight channel. This agrees with the earlier postulations from spectroscopic and modelling characterizations that the protonic acid site is likely to be located in this cross-channel region[19]. As hydrogen atoms can hardly be located using SXPD, a possible simple way to gauge the precise location of the acidic site is by examining the atomic distance and angle between the nitrogen atom in pyridine (as a chemical probe molecule) and the framework oxygen atoms. From the refined structure (see Fig. 2), the inter-atomic distances of the O18 atom to nitrogen atoms in Pyr1 and Pyr2 clearly reflect the atomic location of Brønsted acid site. The calculated N1–O18 distance of 3.61(5) Å and N2–O18 distance of 3.22(3) Å (see Table S3) correspond well with the general

distance of electrostatic interaction between -NH⁺ (PyrH⁺) and the negatively charged O18 (framework). But the anticipated steric repulsion of Pyr1 within the inner smaller sinusoidal channel renders a longer distance than that in the straight channel (see also force field calculations). This is in agreement with the fact that the strong acidic nature of the bridging OH between Al and Si in Al-O18(H)-Si will easily protonate basic adsorbate molecules such as pyridine to form an adduct nitrogen-H⁺ cation. Despite the fact that every Al T-site in zeolite has a first neighboring O shell atoms that are similar in acid strength[30], this experiment clearly shows that the proton actually localizes onto the specific oxygen, O18 in this zeolite that spatially binds with the pyridine molecule strongly. For the second adsorbed pyridine molecule, the N1-N2 distance of 3.41(6) Å falls typically within the regime of hydrogen bonding interactions as PyrH⁺···Pyr where the PyrH⁺ acts a 'secondary' Brønsted acid site. Notice that the higher number of site occupation factor (SOF) of 0.320 in Pyr2 than Pyr1 (0.230) at 100 °C (as well as the SOF values) suggests the co-existence of monomer (Pyr2 only) apart from the dimer structure.

It is noted that by taking symmetry (number of equivalent positions: 8) and the total SOF for both Pyr2 monomer and dimer ratio at room temperature (0.478 + 0.224 = 0.702) into account, 5.62 pyridine molecules were derived from the statistic refinement of the H-ZSM-5 crystal. This corresponds to ca. 1.40 pyridine molecules per as-unit, which matches well with the ca. 1.33 pyridine molecules per as-unit obtained from TGA within experimental errors. In addition, the 1:2 ratio of Pyr2 in dimer to monomer derived from the SOF values also agrees with the peak fit of the DTG data (see Fig. S6). Upon heating, as shown in TGA (see Fig. S6(a)) and in situ SXPD data (see Table 1), Pyr2 located closer to the straight channel in the dimer form appears to be preferentially desorbed (E_a = 24.93 kJ mol⁻¹) at above 100 °C (the SOF ratio becomes close to 1:1 at 200 °C). This would leave behind only two monomer forms before their final desorption at higher temperature (E_a = 39.85 kJ mol⁻¹). Thus, taking entropy factor into consideration, Pyr2 located closer to the more spacious straight channel is likely to be the kinetic intermediate site before filling or unfilling of other sites.

We have also carried out data refinements at various temperatures based on our in situ SXPD data (see Fig. 1B and Table 1). Owing to the increase in disorders in the structure by thermal motions and the decrease in SOF by desorption of pyridine at high temperatures, the changes in bond distances and angles should be treated carefully. Although there are clear fluctuations in the atomic positions of the adsorbed pyridine molecules, it is interesting to note that the N1-O18 and N2-O18 distances and angles remain almost unchanged from 25 °C to 100 °C within experimental errors (see Table 1).

Table 1. Table displaying SOF values, N1-O18, N2-O18 and N1-N2 distances at various temperatures.

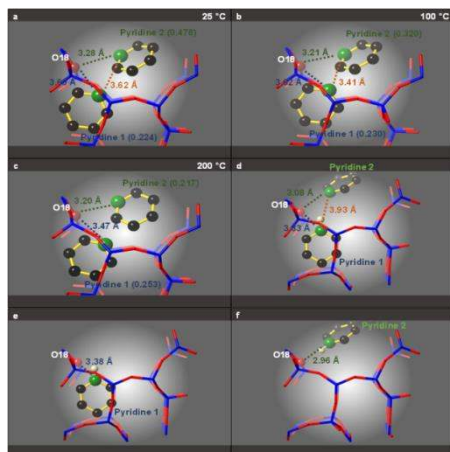| Temperature	25 °C	100 °C	200 °C	300 °C	400 °C
SOF (Pyr1)	0.224(2)	0.230(2)	0.253(2)	0.187(4)	0.137(3)
SOF (Pyr2)	0.478(2)	0.320(2)	0.217(2)	0.084(4)	0.067(3)
N1-O18 (Å)	3.60(4)	3.61(5)	3.47(4)	3.51(5)	3.71(5)
N2-O18 (Å)	3.28(4)	3.22(3)	3.20(6)	3.83(6)	4.40(7)
N1-N2 (Å)	3.62(6)	3.41(6)	-	-	-
R_{wp} (%)	8.663	8.185	7.721	7.371	7.486
χ^2	1.796	1.695	1.601	1.524	1.544

Figure 3 (a-c) Refined crystal structures of H-ZSM-5 with pyridines from 25 °C to 200 °C, and calculated positions of pyridine dimer ([Pyr1H⁺···Pyr2] in (d)); pyridine monomer near sinusoidal channel ([Pyr1H⁺] in (e)); pyridine monomer near straight channel ([Pyr2H⁺] in (f)) by force field modelling. Atoms are represented as: blue sticks = Si/Al, red sticks/balls = O, green balls = N, black balls = C. The values in brackets refer to site occupation factor (SOF).

As shown in Fig. 3 and Table S3, our SXPD refined crystal structure measured at 100 °C suggests: for pyridine 1, N1-O18 = 3.62(4) Å with $\angle$X1-N1-O18 = 100.4(16)°; for pyridine 2, N2-O18 =3.22(4) Å with $\angle$X2-N2-O18 = 135.0(16)°, where X1 and X2 refer to the center of pyridine. A simple modelling calculation using the corresponding force field potential energy of atoms were initially carried out to compare these refined structures from our SXPD data with calculated values although more vigorous modelling (e.g. DFT, QM/MM, ONIOM) at quantum mechanical level could be used. The best fit calculations were based on the simulation of protonation of either one of pyridine molecules by the Brønsted acid site, giving a pyridinium ion, which links with the other pyridine molecule through H-bonding interaction (see Fig. 3(d)). Note that the calculated N1-O18 distance of 3.33 Å with $\angle$X1-N1-O18 angle of 113.6° and the pyridine 2 with N2-O18 distance of 3.08 Å with $\angle$X2-N2-O18 angle of 143.0° are indeed in good agreements with the experimental data by this simple calculation. Their small discrepancies, i.e. ~10% longer bond distances of experimental data at 100 °C, could be accounted for by the difference in the thermal factors between experimental and theoretical calculations. The values for the calculated N1-O18 distances of Pyr1 monomer presented in Fig. 3(e) and the N1-O18 of Pyr2 monomer (see Fig. 3(f)) remain almost unchanged as in the dimer model. This suggests the weak H-bonding interaction in the dimer model only seems to affect the the bond angle (Fig. S9) and orientation slightly but has marginally effects on N-O distances. Notice that the Rietveld refinement data of ammonia at 100 °C clearly suggests that the two adsorption mechanisms are nearly identical: NH$_4^+$ located near sinusoidal channel with related geometry to the pyridine (ammonia 1) which also interacts with negatively charged O18 with the closest N1-O18 distance (see Table S4 and Fig. S4). But, the ammonium ion links with two additional ammonia molecules, forming a trimer through hydrogen bonding, one in the neighbor sinusoidal site (ammonia 2) and the other in a similar position to Pyr2. This opens up the question why no electron density of pyridine is identified in the equivalent neighbor sinusoidal site as in the

case of ammonia 2 at equilibrium position. Apart from the weaker acidity of pyridinium ion, the steric effect of pyridine is thought to be the key factor. The rationalization of bonding and steric interactions of substrates with the acid sites is crucially important in design of zeolites for acid-catalyzed reactions. Therefore, the geometry for adsorption and interactions for stabilization of enzyme-like activated H⁺-guest complex with respect to other adsorbate(s) in zeolite should be considered.

In conclusion, due to the high quality of SXPD data and large number of resolved observables in Rietveld refinement, the atomic positions and angles of adsorbate molecules such as pyridine and ammonia in H-ZSM-5 can be determined within experimental errors. Thus, this study illustrates the preliminary but fundamental approach to establish simple molecular dwell sites on isolated acid site in H-ZSM-5 before using complex zeolite structures or high Al/Si ratios. We believe the generic establishment of atomic positions of adsorbed structure in H-ZSM-5 and related structures could help chemists to understand molecular adsorption and catalytic reactions in confined space.

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Atomic positions and interactions between pyridine molecules and H-ZSM-5 are revealed for the first time in the confined cavity. This is achieved by making use of periodical lattice of H-ZSM-5 (one Brønsted acid site per asymmetric unit) as a template for the trapping of the molecules, with accurate structural elucidation by *in situ* synchrotron powder X-ray diffraction combined with Rietveld refinement within experimental error.
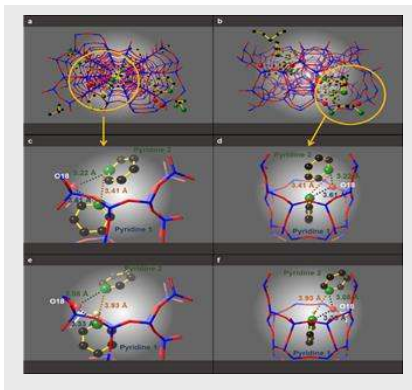
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