

Probing Ethanol Dehydration with Silicon-Doped Aluminophosphates under Realistic Working Conditions Using Inelastic Neutron Scattering and Infrared Measurements

Matthew E. Potter,* Dmitry I. Sharapa,* Maciej G. Walerowski, Hamish Cavaye, Robert Raja, Lindsay-Marie Armstrong, Marina Carravetta, and Felix Studt



Cite This: <https://doi.org/10.1021/acscatal.6c02273>



Read Online

ACCESS |



Metrics & More



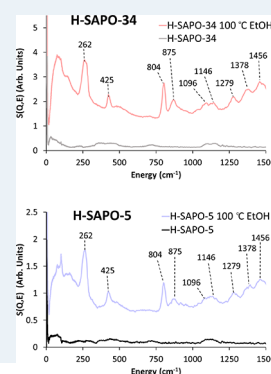
Article Recommendations



Supporting Information

ABSTRACT: Vibrational techniques such as infrared spectroscopy and inelastic neutron scattering offer complementary information into reagent–catalyst interactions. While infrared spectroscopy emphasizes modes with strong changes in dipole moment, inelastic neutron scattering highlights vibrational modes, which displace hydrogen atoms, independent of the effect on dipole moment. In this study, findings from these techniques were combined to probe the interactions of ethanol with two distinct silicon-doped aluminophosphate frameworks, enabling direct comparisons on their reactivity and catalytic mechanisms for ethanol dehydration. By mimicking actual reaction conditions and correlating with reactivity data, these *in situ* and *operando* measurements highlighted the different behaviors of the two catalysts. Furthermore, detailed computational calculations supported the assignment of spectral features, providing a detailed understanding of ethanol dehydration over these materials.

KEYWORDS: spectroscopy, neutron scattering, infrared, theoretical, acid catalysis, porous materials



INTRODUCTION

To prevent irreversible climate damage, there is an urgent need to establish sustainable alternatives to finite fossil fuel feedstocks. This has led many to consider alternative chemical pathways to fulfil demands for chemicals and fuels. In this venture, C_1 and C_2 feedstocks, such as methanol^{1–3} and ethanol,^{4,5} are of great interest as platform chemicals, due to the wide range of possible products and potential green supply chains they can form.⁶ While green methanol requires a demanding CO_2 hydrogenation step,^{7,8} bioethanol is prevalent.^{9,10} Bioethanol is a potential platform chemical for supplying ethylene,^{11,12} diethyl ether,^{13,14} butanol,^{15,16} and acetaldehyde^{9,17} for many chemical processes. Yet, currently, more than 98% of global ethylene production comes from steam cracking of fossil fuels.^{18,19} For ethanol to ethylene to be globally implemented, the dehydration process must be optimized to compete with established fossil fuel methods.²⁰

Solid acid catalysts can be selective ethanol dehydration catalysts if both the strength of the acid site and the space around it are controlled.^{21–23} Microporous solid acid catalysts such as zeolites (aluminosilicates) have been widely investigated (Table S1). Here, acid sites sit within the micropores (pore diameter <2 nm), forcing reactions to occur in a confined environment. By choosing from one of many possible zeolite frameworks, the reactive space can be created with near atomic precision, to promote a specific pathway.^{24–26} In zeolites, replacing framework Si(IV) with Al(III) leads to a net-charge imbalance, causing a proton to bind to the species, creating a

Brønsted acid site (BAS).^{27–29} There is a huge interest in modulating the acid site, particularly by introducing dopants into the framework.^{30,31}

Diethyl ether and ethylene are common products from ethanol dehydration with zeolite catalysts. Typically, diethyl ether formation is favored at lower temperatures (<200 °C), whereas increasing the reaction temperature beyond this has prompted an increase in the ethylene yield, leading to speculation that diethyl ether is actually an intermediate in ethylene formation, as shown in our previous work.^{32,33} Increasing the reaction temperature further has been shown to increase yields of aromatic products (benzene, toluene, and xylenes) and represents a potential pathway to fossil fuel replacements.^{34,35} In most cases, small chain hydrocarbons remain the primary product, suggesting that further optimization is required to make this process competitive. Many researchers have shown that ZSM-5 is comparatively selective for ethylene formation, owing to its stronger BASs and confined micropores, favoring smaller products.^{10,21,30} Its catalytic activity can be further improved by introducing mesopores into the framework (creating hierarchical systems).

Received: March 22, 2026

Revised: August 20, 2026

Accepted: August 24, 2026

This was attributed to the mesopores improving access to the active sites in the micropores, while also promoting the effusion of products and thus preventing deactivation through overreaction leading to coking.^{21,36,37}

While zeolites have been widely investigated for ethanol dehydration, silicon-doped aluminophosphates (SAPOs) have also shown promise.^{12,22,32,33,38} Unlike zeolites, aluminophosphates (AlPOs) are made of alternating Al–O–P bonds, forming similar framework topologies to zeolites. Similar to zeolites, substituting a framework P(V) species with a dopant Si(IV) also creates a BAS (Figure S1).³⁹ Previously, we have shown that the SAPO analogue of chabazite, H-SAPO-34 (pore diameter of 3.8 Å), was an active and selective catalyst for ethanol dehydration to ethylene.³² Through a combined experimental and theoretical study, we showed the superior activity of H-SAPO-34, compared to the larger-pored H-SAPO-5 (pore diameter of 7.3 Å) for this reaction. We concluded that this was due to H-SAPO-34 possessing stronger BASs within a smaller micropore, hindering the formation of a diethyl ether by-product and preventing overactivation.^{22,32} We hypothesized that forming surface ethoxy species (SES) was a key step in ethylene formation, whereas in the larger pore-H-SAPO-5 species, it was possible for the reaction to proceed without the SES, leading to higher quantities of diethyl ether. This finding suggested that the reaction selectivity is governed by the initial binding steps, and the potential formation of the SES.²² As such, there has been much interest in investigating this phenomenon both spectroscopically and theoretically in zeolites and SAPO species.

In this vein, various forms of infrared (IR) spectroscopy have been widely used.^{40–43} Primarily, this is driven by the availability of lab-based IR systems and their flexible sample environments, which allow changes in the spectra to be followed as a function of time and temperature. Furthermore, IR is readily combined with analytical devices, such as mass spectrometry (MS), so spectral changes can be correlated with product distribution, allowing *operando* measurements to be performed.^{40,41,43} Here, the primary focus is correlating the evolution of intermediate species such as weakly bound ethanol, ethanol dimers, or trimers, and the formation of ethylene and diethyl ether products, with the consumption of BAS. IR has been vital in establishing the existence of SES, which are widely regarded as playing a vital role in ethanol dehydration reactions.^{40,41,43} However, this is often convoluted by many of these species having similar signals, making their differentiation challenging.

Density functional theory (DFT) has recently been applied to ethanol dehydration to investigate the energetics of various potential energy surfaces to understand the reaction mechanism.^{22,44–46} This has led to complementing IR findings with frequencies calculated from DFT.⁴⁷ As such, it is common to focus on a smaller “cluster” of the framework, containing the adsorbate and the acid site, while the rest of the framework is either held static or modeled using a lower level of theory.^{22,48,49} Very recently, Kumar et al. used this approach to consider ethanol binding to BAS on a ZSM-5 species.⁴⁷ Here, the calculated overtone frequencies varied significantly depending on the functional used, with B3LYP proving to be a more reliable functional. Previously, Hemelsoet et al. have also compared the binding of methanol and ethanol on H-SAPO-34 where a smaller cluster was modeled using a higher level of theory compared to the rest of the framework.⁵⁰ By comparing IR and DFT calculations, it was surmised that both methanol and

ethanol bind in a similar way to the BAS of H-SAPO-34, where heating the system with the alcohol formed aromatic species.

Inelastic neutron scattering (INS) is a vibrational spectroscopy technique, like IR, and shows a range of vibrational signals that can also be assigned through DFT calculations. Unlike IR, INS does not adhere to selection rules, and due to hydrogen's large neutron scattering cross section, any mode involving hydrogen is orders of magnitude more intense than ones that do not.^{51–53} This makes INS an excellent technique for probing interactions between hydrocarbons and inorganic species. Several studies have used INS to probe methanol–zeolite interactions in MTH (methanol to hydrocarbon) chemistry;^{51,54} however, ethanol–zeolite (and ethanol–zeotype) interactions have been comparatively unexplored. Work from Strange et al. represents one of the few studies to use INS to probe ethanol interactions with solid acid catalysts, in their work on ethanol dehydration over different alumina phases, though to date there are no reports of INS being used to consider ethanol interactions on zeolites.⁵⁵ In this paper, we present a combined theoretical and spectroscopic study probing the ethanol dehydration mechanism on both H-SAPO-34 and H-SAPO-5, building on our previous catalytic study.^{22,32} Novel insights from both temperature-resolved *in situ* INS and *operando* IR were complemented with DFT calculations to assign the various signals, leading to a clear insight into how the catalytic mechanism can be varied through subtle changes in catalyst design.

EXPERIMENTAL METHODS

DRIFTS

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed as per our previous work in a Harrick high-temperature DRIFTS cell with ZnSe windows attached.⁴¹ The cell was attached to the Thermo Fisher Praying Mantis Diffuse Reflectance Accessory and spectra collected with an Agilent Carey 680 FTIR spectrometer.

50 mg of H-SAPO was loaded into the system, heated to 80 °C under 30 mL/min of helium, at a ramp rate of 10 °C/min, and held for 1 h, without the chiller on, to dry the cell. The helium was kept running at this flow rate throughout the whole experiment. After this, the chiller was turned on, and the system ramped up to 400 °C at a rate of 10 °C/min and held for 1 h to further dry the sample. After 1 h, a spectrum was collected. The system was then cooled down to 30 °C at a rate of 20 °C/min. A scan was taken once at 30 °C. 1 μ L of ethanol was injected into the inlet; after 1 min, a spectrum was collected. 5 min after the injection, another 1 μ L was added until a total of 10 μ L had been injected, at which point the system was left to equilibrate for 10 min and a spectrum collected. Analysis of the outlet gas confirmed that all samples were saturated after the second injection, as detailed by identical peak intensities, with the remaining injections performed for consistency. The system was ramped to 400 °C at a rate of 5 °C/min, with spectra collected at 50 °C and then every 25 °C after this until 400 °C, at which point the system was cooled to 30 °C and a final spectrum collected. All spectra were the sum of 128 scans. The outlet gas was monitored using a Hiden Analytical Quantitative Gas Analyser. The detection threshold for this system is a raw partial pressure of 1×10^{-14} . Data points below this threshold have been excluded to allow greater focus on genuine data points.

INS

Inelastic neutron scattering experiments were performed at the ISIS Neutron and Muon source, Didcot, UK, on the TOSCA instrument,^{56–59} under experiment allocation number RB2220187.⁶⁰ All measurements were collected below 20 K, for at least 1200 μ h

of exposure time. All gas handling was performed at ISIS, using the catalysis gas handling rig.⁶¹ Approximately 20 g of the powdered H-SAPO material was dried in a stainless-steel gas-handling can (Figure S2) for 8 h at 400 °C, under a flow of 100 mL/min of helium, after which the can was sealed. Spectra of the sealed systems were then collected and labeled “Bare”. Each system was dosed with liquid ethanol from an HPLC pump at 0.3 mL/min, into a flow of 200 mL/min of helium at 100 °C for 2 h. Once the ethanol concentration had stabilized, signifying saturation, as determined by on-line mass-spectrometry, the ethanol flow was stopped. This led to 1.2 g of ethanol being introduced to the H-SAPO-5 system, and 3.1 g in the H-SAPO-34, determined by the increase in mass of the sealed system. The system was then sealed by closing all valves, to prevent moisture from the air reaching the sample, and remeasured. Following this, the system was heated to 200 °C (and subsequently 300 °C) under a flow of 200 mL/min of helium for 1 h and then resealed and INS spectra recollected.

DFT

All DFT calculations were performed employing the VASP 6.4.3 code,^{62,63} using the PBE functional,^{64,65} a 400 eV energy cutoff, the D3 correction of Grimme,⁶⁶ and a $1 \times 1 \times 1$ *k*-point sampling, which has been found to be sufficient for the chabazite framework.⁶⁷ A PBE-D level of theory was chosen as a standard approach, with known limitations, for zeolite chemistry⁶⁸ and to be consistent with our previous study.²² Postprocessing of vasprun.xml files for INS spectra was performed in MantidWorkbench using the Abins algorithm.^{69–71} All structures were fully optimized, and vibrations were calculated for all atoms. Frequency calculations were performed based on the structures from the geometry optimization. An example of an INCAR file for frequency calculations and the MantidWorkbench script can be found in Figure S3.

In simulations of IR-spectra, the ASE software package⁷² was used to calculate intensities. In this case, vibrations were calculated only for organic molecules, bridging OH groups, and Si/Al atoms directly connected to them. Vibrations were calculated using the finite difference method with a displacement 0.01 Å in all three Cartesian directions (*x*, *y*, *z*). Examples of ASE-script calculations can be found in the Supporting Information. Only peaks in the region 2750–3100 cm^{−1} are of interest and were scaled according to equation $(0.5764 \cdot x) + 1213.6$ (where *x* is the DFT-simulated position), which was obtained by fitting of DFT-derived IR vibrations with those experimentally obtained for gaseous ethanol and diethyl ether. We note that this linear fitting was performed exclusively to get accurate agreements in the 2750–3100 cm^{−1} region of interest. If the full spectral range was used, the scaling factor would instead be 0.9915 (see Figure S4). Peaks are plotted with Lorentzian broadening and a full width at half maximum (FWHM) of 20 cm^{−1}. The dipole moments of calculated systems are known to be highly sensitive to small deviations in the orientation of adsorbants, and dipole moments of different zeolite can vary greatly. As a result, the intensity of calculated IR signals is very sensitive to subtle numerical errors and instabilities, and for this reason, the precise intensities should be treated with caution.

Structures of SAPO-34 and SAPO-5 are identical to those published in our previous work,²² with SAPO-34 as hexagonal (*a* = *b* = 13.875 Å, *c* = 15.017 Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) and SAPO-5 as hexagonal also (*a* = *b* = 13.863 Å, *c* = 15.017 Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$). The protonation site was chosen in agreement with the wider literature.⁷³ All structures are provided in the Supporting Information (SI).

RESULTS AND DISCUSSION

Sample Integrity

H-SAPO-34 and H-SAPO-5 were synthesized according to our previously published protocols (see the Supporting Information

for synthesis details), with consistent characterization data to our previously published work, confirming batch reproducibility.^{22,33,41} A more detailed discussion of the physicochemical characteristics of these materials has been previously published, but we provide a summary here.²² Powder X-ray diffraction (Figure S5) confirmed that only peaks associated with the expected frameworks were present (CHA for H-SAPO-34 and AFI for H-SAPO-5). This confirmed the phase purity of the systems, with unit cell parameters in good agreement with published values (Table S2).²² BET analysis (Figure S6 and Table S3) showed that H-SAPO-34 had a higher surface area (537 m² g^{−1}) than H-SAPO-5 (240 m² g^{−1}), agreeing with similar systems in the literature.²² H-SAPO-5 had a lower silicon content (2.5 wt %) than H-SAPO-34 (3.7 wt %), as different frameworks can only accommodate a limited range of silicon loadings while still forming phase pure materials (Table S3). Scanning electron microscopy (SEM) images (Figure S7) show H-SAPO-5 as hexagonal crystals, whereas H-SAPO-34 presents as cubic crystals, in agreement with their crystallographic point groups.²² ²⁷Al and ³¹P solid-state nuclear magnetic resonance (ssNMR) confirmed that tetrahedral AlO₄ (Figure S8a) and PO₄ (Figure S8b) were the dominant species in both cases. ²⁹Si ssNMR (Figure S8c) suggested that the silicon in H-SAPO-34 was the isolated framework-substituted Si(OAl)₄ species. H-SAPO-5 showed a shift to lower ppm, suggesting fewer isolated sites, and more Si–O–Si bonds forming. Ammonia temperature-programmed desorption (NH₃-TPD) measurements (Figure S9) showed that H-SAPO-34 had significantly more acid sites than H-SAPO-5, in line with H-SAPO-34 having a greater proportion of isolated silicon species, and its higher silicon loading (Table S4). The acid sites in H-SAPO-34 are also notably stronger than those in H-SAPO-5.

DRIFTS measurements collected at 30 °C after drying at 400 °C probed the initial acid sites in both H-SAPO-34 and H-SAPO-5 (Figure S10). After drying at 400 °C, the H-SAPO-34 DRIFTS shows a characteristic double signal at 3625 and 3600 cm^{−1} attributed to Al–OH–Si signals with varying degrees of hydrogen bonding in the CHA system. This system also shows a subtle signal at 3676 cm^{−1} attributed to defect Al–OH groups. The H-SAPO-5 system shows broad signals at 3517 and 3625 cm^{−1} again attributed to Al–OH–Si systems with varying degrees of hydrogen bonding. There is a great concentration of hydroxyl defect sites in the H-SAPO-5 species, with clear features at 3741 and 3670 cm^{−1} attributed to defect Si–OH and Al–OH species, respectively.

Our previous catalytic data of both species showed that at lower temperatures (170 °C; Figure S11a), H-SAPO-34 was more active than H-SAPO-5, achieving a higher ethanol conversion and ethylene selectivity.²² Increasing the temperature so that both systems had comparable conversion (200 °C; Figure S11b) showed that H-SAPO-34 primarily formed ethylene (59% selectivity), whereas H-SAPO-5 primarily formed diethyl ether (87% selectivity). The trend of H-SAPO-34 having higher (or comparable) ethanol conversion than H-SAPO-5, and H-SAPO-34 having a greater preference for ethylene formation over H-SAPO-5, was seen across a range of temperatures (155–200 °C) and WHSV (weight hourly space velocity; 1.0–2.0 h^{−1}).

INS

INS spectra of dried H-SAPO-34 and H-SAPO-5 were found to contain few, weak features (Figure 1), owing to the small

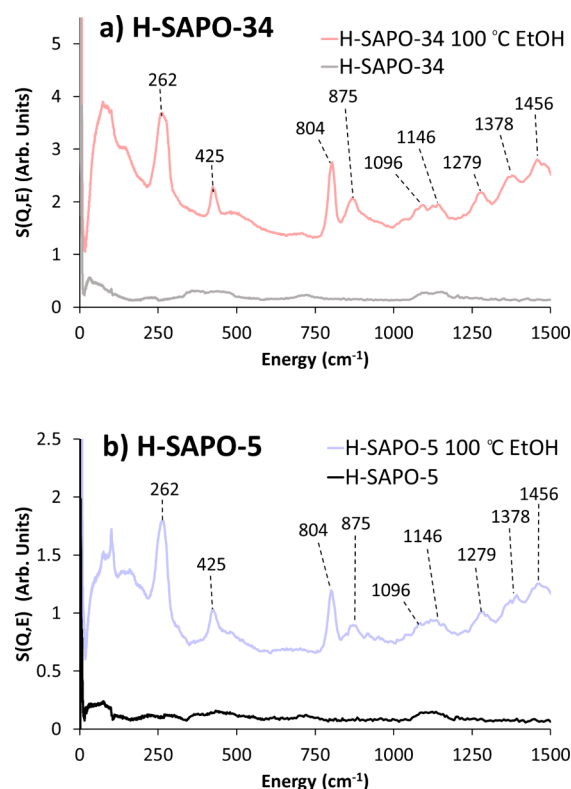


Figure 1. INS spectra showing the influence of adding EtOH to (a) H-SAPO-34 and (b) H-SAPO-5, after heating EtOH to 100 °C.

quantities of hydrogen present in these systems. Furthermore, TOSCA is optimized to focus on signals below 2000 cm^{-1} and loses sensitivity above this region.^{56–58} As such, the characteristic OH stretches commonly associated with H-SAPO (and zeolite systems) between 3500 and 3800 cm^{-1} were not visible.

Liquid ethanol was then introduced into a flow of 100 mL/min of helium separately to both systems while heated at 100 °C (Figure S12). The system was then sealed to prevent moisture entering the system and cooled, and INS spectra were recollected. After the addition of ethanol at 100 °C, the INS signals of both H-SAPO-34 and H-SAPO-5 became more intense (Figure 1), due to the hydrogen from ethanol now being present. Both the initial H-SAPO-34 100 °C and H-SAPO-5 100 °C INS spectra (where the temperature refers to the highest temperature the system was exposed to before measurement) showed smooth, well-defined peaks, in good agreement with the solid ethanol spectra from Strange et al. and the TOSCA database (Figure S13).^{55,74} Here, the H-SAPO-34 spectrum was more intense than the H-SAPO-5 system, due to the greater quantity of ethanol present in the system (3.1 g in H-SAPO-34 vs 1.2 g in H-SAPO-5). The differing ethanol uptake is likely a result of the greater surface area of H-SAPO-34 (537 $\text{m}^2 \text{g}^{-1}$) compared to H-SAPO-5 (240 $\text{m}^2 \text{g}^{-1}$), allowing H-SAPO-34 to adsorb a greater quantity of ethanol. This is supported by the ethanol uptake per surface area being similar for the systems, with H-SAPO-34 taking up 0.0057 $\text{g}_{\text{EtOH}} \text{ per m}^2 \text{g}^{-1}$ and H-SAPO-5 taking up 0.0050 $\text{g}_{\text{EtOH}} \text{ per m}^2 \text{g}^{-1}$.

Notably, both spectra showed a strong initial signal at 262 cm^{-1} assigned to methyl torsions and a further signal at

425 cm^{-1} .⁵⁵ A pair of peaks follow at 804 and 875 cm^{-1} assigned to C–O–H bending⁷⁵ and C–C stretches, respectively.⁷⁶ Signals at 1096 and 1146 cm^{-1} follow, both assigned to C–O and C–C stretches modes, respectively.⁷⁷ Finally, the H-SAPO-34 system dosed with ethanol shows a trio of well-defined features at 1279, 1378, and 1456 cm^{-1} , corresponding to C–H bending, symmetric methyl bending, and asymmetric methyl bending, respectively.^{55,77} The spectra after treatment at 100 °C strongly resembled solid ethanol, suggesting that the majority of ethanol present was currently either very weakly adsorbed or nonadsorbed.

The ethanol-H-SAPO-34 system was then heated to 200 °C under a flow of 100 mL/min of helium for 1 h, with no further ethanol added. The system was then resealed, and the spectra recollected (Figures 2 and Figure S14).

This system showed a range of new features, notably at 312, 375, and 503 cm^{-1} (Figure S14a). The methyl torsion signal shifted downward from 263 to 255 cm^{-1} , and the signal at 427 cm^{-1} shifted upward to 438 cm^{-1} . The 804 cm^{-1} C–O–H bending mode also shifted upward to 812 cm^{-1} . Notably, the C–C stretch at 875 cm^{-1} greatly diminished. This deviation from the “solid ethanol” spectra clearly indicates that the ethanol is no longer weakly bound and is either interacting more strongly with the H-SAPO-34 framework or has undergone a transformation. There was only a very modest decrease in overall intensity between the 100 and 200 °C H-SAPO-34 spectra. The spectral intensity of INS is directly proportional to the quantity of hydrogen atoms in the system and as such is often treated as a hydrogen molar balance. As such, we can conclude that the vast majority of hydrogen atoms remain in the H-SAPO-34 system. This confirms that minimal amounts of weakly bound ethanol have been desorbed and left the system or formed products, which then diffused out from the system. We note that the spectra do not show any significant signs of water binding, which in similar zeolite systems would present as a broad feature between 400 and 800 cm^{-1} . Similarly, the system is free from ice, which would present as a sharp feature around 550 cm^{-1} .⁷⁸ Difference spectra confirmed the minimal decrease in baseline intensity as the temperatures increased, confirming that similar quantities of hydrogen-containing species were present in all cases (Figure S14c). Focusing on the 0–500 cm^{-1} region (Figure S14d) shows that the most significant decreases are at roughly 277 and 425 cm^{-1} . Signals emerge at 232 cm^{-1} , particularly in the 300 °C spectra, suggesting that some chemical transformation is occurring.

DFT calculations were performed to identify the emerging signals in the H-SAPO-34 system upon heating (Figure 3).

The INS spectra (Figure 3a and Figure S15) were calculated using optimized geometries of diethyl ether, ethanol, and the hypothesized SES (Figure 3b–d). The SES species aligned particularly well with the experimental INS findings. Notably, the experimental INS data showed that the broad feature between 50 and 100 cm^{-1} shifted to lower energy as the temperature increased, in good agreement with the calculated SES data, which showed an emerging signal at 45 cm^{-1} . The emerging shoulder at 233 cm^{-1} in the experimental data aligned well with the predicted feature at 231 cm^{-1} in the SES data that corresponds to a rotation of the methyl group (and also shows an intensive H-spectrum that is simultaneously C-silent). Furthermore, only the SES species display any features within the 300–400 cm^{-1} range, best described as the SES species gyrating from side to side, where we observed significant

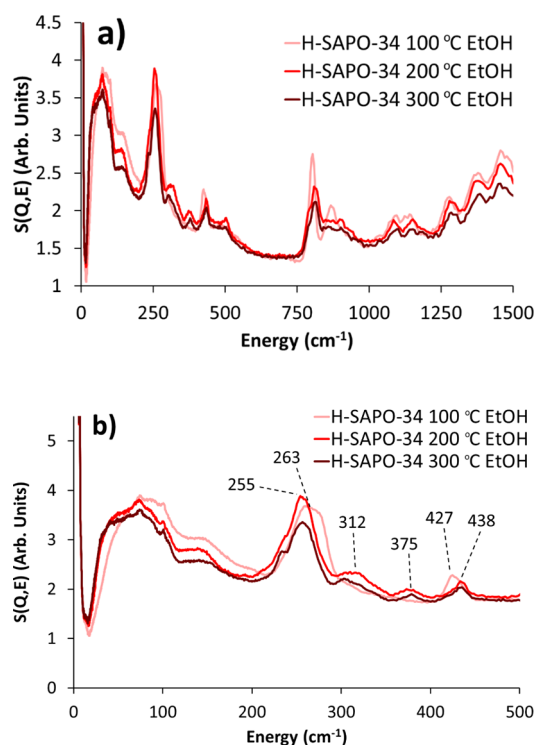


Figure 2. INS spectra of ethanol-H-SAPO-34 systems after heating to a range of temperatures (a) showing the wider spectra range (0–1500 cm⁻¹) and (b) focusing on the lower energy range (0–500 cm⁻¹).

experimental features emerging. It is further noted that the signals from the diminishing signals identified in the difference spectra (Figure S14d; 277 and 425 cm⁻¹) correspond to predicted signals from H-SAPO-34 and ethanol, whereas the emerging signal at 232 cm⁻¹ strongly aligns with the predicted SES spectra. As such, the features that emerged as the experimental INS system deviated from solid ethanol were in excellent agreement with a SES forming on the H-SAPO-34 system. The ethanol-bound species in SAPO-34 were confirmed through analogous ssNMR (Figure S16) experiments of isotopically labeled ¹³C₂-ethanol loaded onto a similar H-MgSAPO-34 material at room temperature. The resulting experimental NMR spectrum showed two pairs of signals at 16 and 17 ppm, and also at 57 and 61 ppm. Using optimized DFT geometries of various ethanol species to predict ¹³C NMR peak positions, these features were predicted to be a combination of gas-phase ethanol and ethanol interacting with H-SAPO-34, which were found to account for the signals, in good agreement with the INS data above.

The ethanol-H-SAPO-34 system was then progressively heated to 300 °C, again under a flow of 100 mL/min of helium, with no added ethanol. This also showed only another very modest drop in intensity, again suggesting most of the hydrogen atoms have been retained (Figure 2 and Figure S14). There was also an excellent agreement between the 200 and 300 °C H-SAPO-34 spectra. This suggests that the bound-ethanol species formed at 200 °C either remained strongly bound to H-SAPO-34 despite experiencing higher temperatures or were repeatedly readsorbed throughout the large sample bed. The latter would likely lead to readsorption and reformation

once the sample cooled down for INS measurements below -253 °C (20 K). The combined DFT and INS study confirms that very few of the hydrogen atoms (from ethanol) introduced initially at 100 °C to the H-SAPO-34 system have left the system, even after heating to 300 °C. The data suggests that the ethanol is initially weakly bound at 100 °C. At 200 °C, this ethanol becomes strongly bound to the system, likely as an SES, based on our DFT assignments. For ethanol to convert to an SES on an acid site, water must also form to balance the chemical equation. We do not see any obvious signs of water formation such as evolving peaks at 400 or 650 cm⁻¹ associated with adsorbed water or ice.⁷⁹ However, such species are characteristically broad even in simple systems. Despite this, given the consistent spectral intensity, we must conclude that water must also be retained in the system.

Analogous studies were performed on H-SAPO-5. Unlike H-SAPO-34, heating the ethanol-dosed H-SAPO-5 system to 200 °C showed only very subtle variation, showing that H-SAPO-5 retains a significant quantity of the weakly bound ethanol (Figure 4 and Figure S17).

This similarity suggests minimal chemical transformation, and thus minute formation of water. Only very subtle new features appeared at 224 and 315 cm⁻¹, accompanied by the methyl torsion shifting downward from 264 to 259 cm⁻¹.⁵⁵ However, the most significant change was the flattening and broadening of the features between 750 and 1000 cm⁻¹ (Figure S17a), indicating increasing structural disorder and reduced spectral resolution of the associated vibrational modes. The signal at 427 cm⁻¹ shifted upward to 433 cm⁻¹, and finally the C–O–H bending mode at 804 shifted upward to 808 cm⁻¹.^{55,75} The more subtle peak shifts compared to H-SAPO-34 were likely due to bound ethanol in H-SAPO-5 either being less confined. As such, the less confined species could have less restricted molecular motion, closer to bulk ethanol, and fewer interactions with the micropores, resulting in a smaller deviation from the weakly bound system. The intensity of the ethanol-H-SAPO-5 system was again similar between 100 and 200 °C, again suggesting that most of the ethanol has remained (bound) in the system. None of the DFT-calculated INS spectra of H-SAPO-5 with SES, ethanol, and diethyl ether species interacting with the acid site showed notable signals in the 315 cm⁻¹ region (Figure S18), making it more likely that these subtle variations are not due to interactions with the acid site. More likely, this is a result of the confined ethanol interacting with the pore walls at the very low temperatures measured within the catalyst, partly due to the lower number of BAS per unit mass of H-SAPO-5 (Table S4). The difference spectra for H-SAPO-5 at 200 °C (Figure S17c) also confirm that minimal change has occurred.

The spectra collected after heating ethanol-H-SAPO-5 to 300 °C showed a notable decrease in intensity (Figure 4), as confirmed by the difference spectra (Figure S17c). This loss of hydrogen signal suggested that unlike H-SAPO-34, either a significant quantity of ethanol has desorbed or it has formed products that have then desorbed. As with H-SAPO-5, the most notable decreases were around 269 and 422 cm⁻¹ (Figure S17d), though at 300 °C, there were no notable emerging signals. Our previous work showed that H-SAPO-34 consistently demonstrated higher ethanol conversions than H-SAPO-5, under identical catalytic conditions. Hence, despite H-SAPO-34 being more active, it was H-SAPO-5 that showed the greatest loss of hydrogen-containing molecules. This can be rationalized by considering the differences between the catalytic conditions and the *in situ* treatments in the INS experiments.

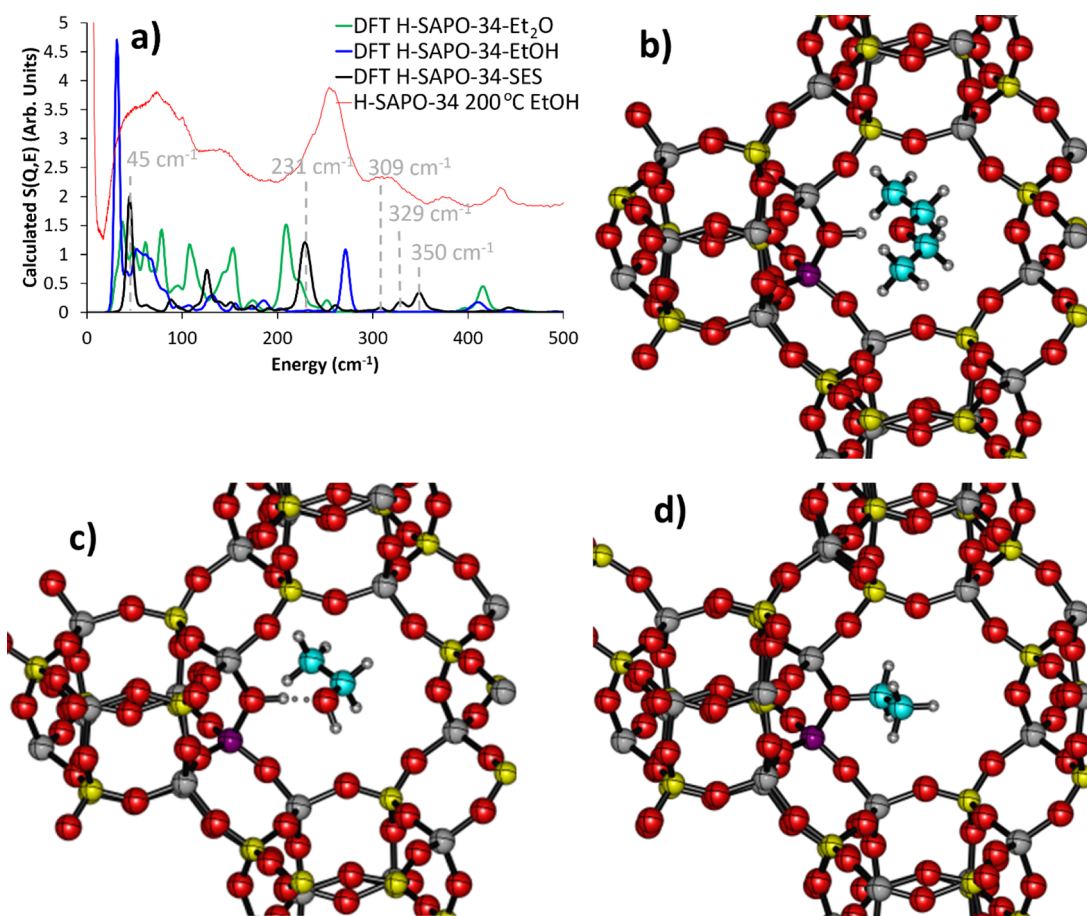


Figure 3. (a) Calculated INS spectra of potential diethyl ether (Et_2O), ethanol (EtOH), and surface ethoxy species (SES) H-SAPO-34 systems, compared with the experimental spectra, focusing on the low energy region ($0\text{--}500\text{ cm}^{-1}$). (b) Calculated structure used for H-SAPO-34 Et_2O , (c) H-SAPO-34-EtOH, and (d) H-SAPO-34 SES.

The differing GHSV (gas hourly space velocity) was a significant factor. Under catalysis conditions, the GHSV is approximately $100\text{ mL min}^{-1}\text{ g}_{\text{cat}}^{-1}$. However, under INS conditions, the gas flow must be limited to prevent pressure buildup through the larger powdered catalyst bed; as such, the GHSV was approximately $5\text{ mL min}^{-1}\text{ g}_{\text{cat}}^{-1}$, a factor of 20 lower. Our previous work confirmed that ethanol, diethyl ether, and ethylene diffuse more rapidly through the H-SAPO-5 framework than H-SAPO-34 by at least an order of magnitude. As such, it is likely that the lower GHSV in the INS treatment would have hindered the already slower effusion of ethanol, diethyl ether, and ethylene from the smaller-pored H-SAPO-34 system to a greater extent than the H-SAPO-5 system. Furthermore, the INS findings suggest that a greater quantity of weakly bound ethanol existed at $200\text{ }^\circ\text{C}$ in the H-SAPO-5 system, than H-SAPO-34. This may have expedited the formation of diethyl ether in the H-SAPO-5 system, which readily diffused out of the system.⁴¹ It is likely also that not constantly flowing ethanol through the system may have caused some deviation between the INS and catalytic conditions, particularly for H-SAPO-5, which per unit mass possessed both a lower surface area and lower acid site density than H-SAPO-34 (Tables S3 and S4), limiting the interactions between the sorbate and catalyst. However, this was unavoidable given the INS data collection conditions.

Therefore, the INS data was consistent with the ethanol and intermediates being more confined within the H-SAPO-34 pores, leading to them being retained at higher temperatures. In contrast, the bound ethanol species in H-SAPO-5 either desorbed more readily, or reacted more effectively, but crucially were able to diffuse out through the large, powdered bed. In both H-SAPO-5 and H-SAPO-34, an effective transition from weakly bound or nonbonding ethanol to strongly bound ethanol species was observed between 100 and $200\text{ }^\circ\text{C}$.

DRIFTS

To gain more detailed insight into the process, a complementary *operando* DRIFTS study was performed on these systems to probe the reactive intermediates in greater detail. The experimental spectra were firstly informed by DFT calculations to predict the spectra of different potential species.

The H-SAPO-34 ether spectrum (Figure 5, green, assignments in Table S5) had its dominant feature at 2937 cm^{-1} (symmetric stretching in CH_2), with smaller features at 2972 (asymmetric C–H stretching in CH_3), 2889 (symmetric stretching in CH_2), and 2866 cm^{-1} (asymmetric stretching in CH_2). In contrast, the ethanol species (Figure 5, blue, assignments in Table S6) had a primary feature at 2919 cm^{-1} (symmetric stretching in CH_2), with smaller features at 2947 (asymmetric stretching in CH_2) and 2971 cm^{-1} (asymmetric

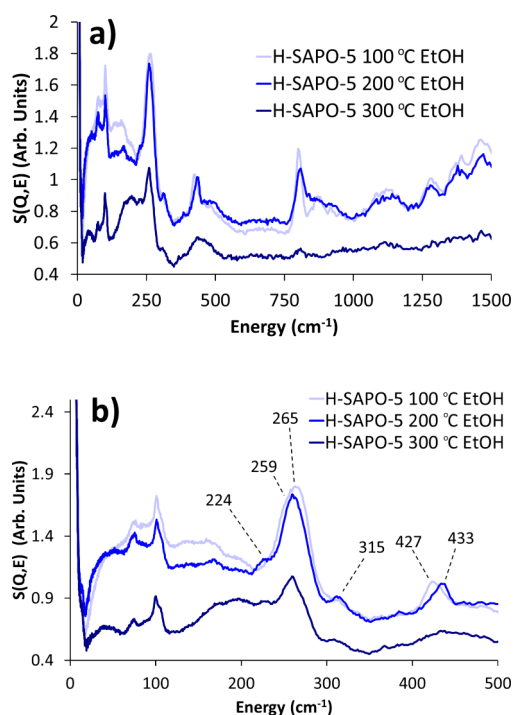


Figure 4. INS spectra of ethanol-H-SAPO-5 systems after heating to a range of temperatures (a) showing the wider spectra range (0–1500 cm^{-1}) and (b) focusing on the lower energy range (0–500 cm^{-1}).

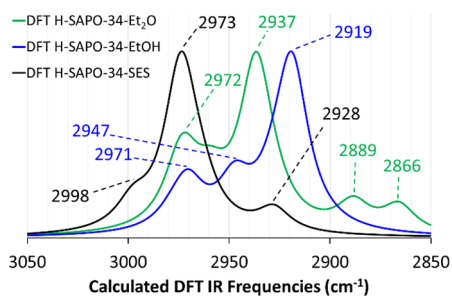


Figure 5. DFT-calculated IR frequencies for H-SAPO-34 species including bound ether (green), bound ethanol (blue), and SES (black). Assignments in Tables S5–S7.

C–H stretching in CH_3) with no calculated features between 2900 and 2800 cm^{-1} . Finally, the calculated SES spectrum (Figure 5, black, assignments in Table S7) had its dominant feature at a frequency of 2973 cm^{-1} (complex convolution of three C–H stretchings) with a notable shoulder at higher wavenumbers: 2998 cm^{-1} (asymmetric stretching in CH_2) and finally a further signal at 2928 cm^{-1} (symmetric C–H stretching in CH_3). No other signals were observed in the 3100 to 2800 cm^{-1} region. As per our previous work, we excluded water from the calculations of the stable surface species.²² We note, however, that even the most advanced computational codes often result in misleading intensities for IR signals. As such, going forward, we place greater emphasis on the position of calculated IR signals, and the absence of peaks, instead of the absolute intensity of such features.

For the DRIFTS measurements, 50 mg of each dried H-SAPO catalyst was saturated with a total of 10 μL of ethanol, delivered in ten 1 μL injections, under a 30 mL min^{-1} helium flow at 30 $^\circ\text{C}$, leading to a GHSV of 600 $\text{mL min}^{-1} \text{g}_{\text{cat}}^{-1}$ (Figure 6a). On-line mass spectrometry confirmed that the system was saturated as, beyond the first injection, the signals displayed a consistent intensity, confirming saturation (Figure S19). The dosing data was also used to determine the relative contributions of each fragment ($M/Z = 59, 31$, and 27) from diethyl ether, ethanol, and ethylene. This allowed the total intensity of these signals to be deconvoluted into the relative concentrations of each species; see the Supporting Information for further details. Once the excess ethanol had left the system, the temperature was then ramped at 5 $^\circ\text{C/min}$ while DRIFTS spectra were collected focusing on the 3100–2800 cm^{-1} region (Figure 6a), the 1500–1000 cm^{-1} region (Figure S20a,b), and the 4000–3200 cm^{-1} region (Figure S20c). The varying baseline in the 1500–1000 cm^{-1} region made it challenging to clearly identify the more subtle features (Figure S20a). As such, this data is also presented where the data from 30 $^\circ\text{C}$, the initial data point of the temperature, has been subtracted (Figure S20b).

H-SAPO-34 initially showed four signals in the C–H region, a main signal at 2979 cm^{-1} , and three smaller signals at 2936, 2906, and 2877 cm^{-1} , in good agreement with the work from Kumar et al.,⁴⁷ which they assigned to ethanol molecules in the H-ZSM-5 zeolite. However, evidence from Matam et al.⁸⁰ suggests that surface alkoxy groups can form on H-ZSM-5 under similar conditions, something not investigated by Kumar et al. but is central to the current study on H-SAPO-34. Given the similar location of SES and ethanol signals, it is challenging to definitively assign features based on a single spectrum, and as such, the assignments are also guided by the spectral changes with temperatures.

The position of the first two signals (2979 and 2936 cm^{-1}) show some similarity to the calculated SES. However, the remaining significant signals (2906 and 2877 cm^{-1}) are likely associated with weakly bounded ethanol, or potentially diethyl ether (as seen in Figure 5).^{41,43,47} The initial spectra are likely a combination of different species, hence the features not all aligning precisely with the frequencies predicted by DFT for one particular species (Figure 5).

At 150 $^\circ\text{C}$, the spectra began to change, with a shoulder feature at 3019 cm^{-1} appearing. A signal with this high a wavenumber is only predicted in the SES spectra, as a shoulder. A relative decrease in the intensity of the 2906 and 2877 cm^{-1} signals is also seen, with signals in this region not predicted for SES, again strengthening the assignment of these spectra beginning to form an SES species. This was mirrored in the 1500–1000 cm^{-1} data (Figure S20a,b) where notable decreases were seen in the 1263, 1220, and 1029 cm^{-1} signals, which have previously been attributed to weakly bound ethanol.⁸¹

This slow progression was likely due to a mixture of weakly bound ethanol and ether and strongly bound ethanol, or most likely SES, residing within the H-SAPO-34 pore. On heating to 250 $^\circ\text{C}$, more notable changes occurred, with the feature at 3019 cm^{-1} becoming more defined, a broader main signal at 2983 cm^{-1} , and a defined peak at 2938 cm^{-1} , with other signals becoming broader and less intense. The 250 $^\circ\text{C}$ experimental IR spectrum strongly resembled the shape of the calculated SES spectrum, validating our computational approach. As such, we suggest that the SES species has been the dominant feature

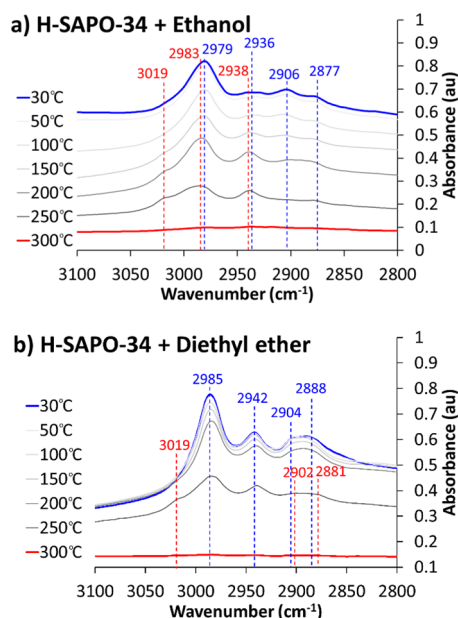


Figure 6. DRIFTS spectra of H-SAPO-34 under *operando* conditions with (a) ethanol and (b) diethyl ether feedstocks.

throughout this data set. While the feature at 3019 cm^{-1} is in good agreement with the shoulder predicted by the DFT-calculated SES spectra, it is possible that this may also be due to the formation of unsaturated species. The $2000\text{--}1500\text{ cm}^{-1}$ region showed significant signal baseline variation with temperature, preventing any complementary features associated with $\text{C}=\text{C}$ bonds being identified. This could be probed in greater detail using UV–vis spectroscopy to explore the formation of larger aromatic products known to form in the ethanol-to-hydrocarbon reactions.

In the $1500\text{--}1000\text{ cm}^{-1}$ region, notable increases were seen in signals at 1475 , 1422 , and 1370 cm^{-1} , which have previously been associated with SES species. These signals grew concurrently with a species at 1066 cm^{-1} , providing strong evidence that this signal is also associated with the SES species. We note also that the signal at 1174 cm^{-1} appears to grow and then declines, which has previously been associated with the methyl rocking in diethyl ether.⁸² At this temperature ($250\text{ }^{\circ}\text{C}$), the acid site signal had largely returned, showing limited interactions with the acid sites. At $300\text{ }^{\circ}\text{C}$, the intensity of all DRIFTS signals in the $3100\text{--}2800\text{ cm}^{-1}$ region has diminished, suggesting that little organic component remained bound to the catalyst, and the acid site signal had recovered. Overall, this study shows that ethanol is initially weakly bound to the system, before converting into SES.

The accompanying online mass spectroscopy (Figure S20d) demonstrated that there were two defined regimes of activity, first from 90 to $170\text{ }^{\circ}\text{C}$, where ethanol and diethyl ether were exiting the system. Then, between 190 and $300\text{ }^{\circ}\text{C}$, there was another release of ethanol and diethyl ether but also the onset of ethylene formation. Correlating this change with the DRIFTS spectra suggested that diethyl ether was only capable of forming when weakly bound ethanol was present in the system. Above $200\text{ }^{\circ}\text{C}$, the DRIFTS spectra primarily showed strongly bound SES species, as all weakly bound species have desorbed, in good agreement with the onset of ethylene formation in the system.^{41,43,47} This

suggests that in H-SAPO-34, it was these strong sites alone that were necessary for ethylene formation. Above $300\text{ }^{\circ}\text{C}$, all signals decreased by an order of magnitude, indicating a reduction of signals from reactants and product molecules.

To probe the origin of the SES species, an identical experiment was performed using diethyl ether as the feedstock (Figure 6b) instead of ethanol. Again, dosing was performed by injecting ten $1\text{ }\mu\text{L}$ injections to saturate the system, as confirmed through the online MS data (Figure S19b). At $30\text{ }^{\circ}\text{C}$, this led to signals at 2985 , 2942 , 2904 , and 2888 cm^{-1} . The signals are in similar positions to the initial IR spectrum with ethanol (Figure 6a), though notably the latter two signals 2904 and 2888 cm^{-1} are more pronounced than the ethanol spectra, in agreement with the predicted spectra of H-SAPO-34 interacting with diethyl ether (Figure 5). The similarity in the diethyl ether and ethanol molecules was also seen in the $1500\text{--}1000\text{ cm}^{-1}$ region, where very similar signals can be observed in the ethanol (Figure S20) and diethyl ether feedstocks (Figure S21). The most striking difference however was the comparatively flat baseline in the $4000\text{--}3200\text{ cm}^{-1}$ region with the diethyl ether feedstock (Figure S21d). This is attributed to the ether molecule not having a hydroxy group, and therefore not experiencing significantly less hydrogen bonding with the acid groups. Very little change was observed in the $3100\text{--}2800$ and $1500\text{--}1000\text{ cm}^{-1}$ regions below $200\text{ }^{\circ}\text{C}$. Some reformation of the acid sites was observed however in the $4000\text{--}3200\text{ cm}^{-1}$ region.

As the system was heated to $200\text{ }^{\circ}\text{C}$, a shoulder again appeared at 3019 cm^{-1} , and the shifting of the final two peaks to 2902 and 2881 cm^{-1} diminished, better resembling the SES spectra. This was accompanied by signals forming at 1486 , 1409 , 1376 , and 1066 cm^{-1} , again attributed to the formation of SES (Figure S21a,b). Notably, the mass spectroscopy trace showed that despite the different feedstock, ethylene formation occurred within a very similar temperature window (Figure S21d). Comparing the H-SAPO-34 DRIFTS data with ethanol and diethyl ether suggests that both feedstocks led to the formation of strongly bound SES species, and it is these SES that form ethylene, independent of the initial feedstock (Figure S21e), as suggested in our previous work.³² The ability to readily form ethylene from both diethyl ether and ethanol is likely a major factor for the superior ethylene selectivity for H-SAPO-34. This is in good agreement with our previous calculations, which suggested that the free energy barriers at $200\text{ }^{\circ}\text{C}$ for the formation of a SES from ethanol (ΔG of 122 kJ mol^{-1} and $\Delta\Delta G$ of 136 kJ mol^{-1}) and diethyl ether (ΔG of 119 kJ mol^{-1} and of $\Delta\Delta G$ of 138 kJ mol^{-1}) were very similar.²² This agrees with our DRIFTS findings that both ethanol and diethyl ether would be an effective initial reagent for both SES and ethylene formation.

H-SAPO-5 was also examined under the same DRIFTS procedures (Figure 7 and Figure S22). Like the H-SAPO-34 species, this showed a main signal at 2980 cm^{-1} , and three smaller signals at 2936 , 2906 , and 2877 cm^{-1} .

Already at $100\text{ }^{\circ}\text{C}$, notable changes occurred in the spectrum, and at $150\text{ }^{\circ}\text{C}$, a clearly defined shoulder occurred at 3017 cm^{-1} , and as with H-SAPO-34, the signal at 2906 cm^{-1} greatly diminished. Furthermore, the main signal at 2988 cm^{-1} lost intensity, as a separate feature at 2992 cm^{-1} emerged, alongside a feature at 2938 cm^{-1} . Increasing the temperature further to $250\text{ }^{\circ}\text{C}$ showed the signals at 2992 and 2938 cm^{-1} becoming the dominant signals; again at $300\text{ }^{\circ}\text{C}$, the signals have largely diminished. The onset of the SES species in H-SAPO-5 occurred earlier than H-SAPO-34, despite H-SAPO-5 being less active. Previous

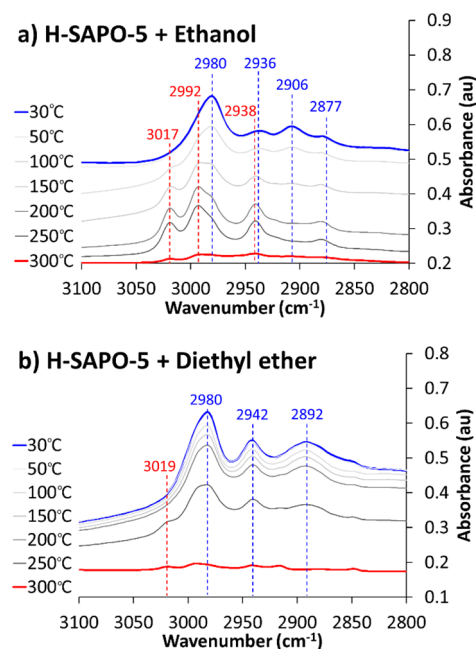


Figure 7. DRIFTS spectra of H-SAPO-5 under *operando* conditions with (a) ethanol and (b) diethyl ether feedstocks.

literature has suggested that surface alkoxy species form rapidly at low temperatures, and as such, SES formation alone may not directly correlate with acid site strength and is more likely correlated with the availability and accessibility of active sites in H-SAPO-5.⁸³

The DRIFTS signal in the 1500–1000 cm^{-1} region was notably less intense in H-SAPO-5 than in H-SAPO-34, with less variation with temperature (Figure S22a,b). Broadly though, the trends align well with the 3100–2800 cm^{-1} region with a notable decrease in signals associated with physisorbed ethanol—1288, 1224, and 1035 cm^{-1} as early as 100 °C. This is accompanied by an emergence of a broad feature between 1470 and 1360 cm^{-1} , due to the early emergence of SES species in H-SAPO-5. The acid site region (Figure S22c) only shows the acid sites reforming after 200 °C.

We anticipate again that this was due to the difference in GHSV between our catalysis, INS, and DRIFTS experiments. In INS, the lower GHSV (5 $\text{mL min}^{-1} \text{g}_{\text{cat}}^{-1}$) meant that the weakly bound ethanol was not desorbed as easily, and as such, we saw a greater fraction of weakly bound/noninteracting ethanol remaining in the INS, whereas the much larger GHSV (600 $\text{mL min}^{-1} \text{g}_{\text{cat}}^{-1}$) in the DRIFTS will be more effective at driving out weakly bound ethanol, leaving just the SES in the H-SAPO-5 system, causing the earlier onset in the DRIFTS. This was in good agreement with the mass spectrometry data, where we saw no diethyl ether formed in the DRIFTS experiment (Figure S22e). This is very likely due to the ethanol species being too isolated as they were anchored to the framework through SES species. Above 210 °C, we began to see ethylene formation in the H-SAPO-5 system, which continued above 300 °C, which coincides with the acid sites reforming (Figure S22c), again suggesting that SES plays a key role in ethylene formation, particularly in the absence of free ethanol to stimulate diethyl ether formation.

H-SAPO-5 was also examined using diethyl ether as a feedstock (Figure 7b and Figure S23). However, with increasing temperature, the only obvious spectral changes were the

evolution of the shoulder feature at 3019 cm^{-1} , suggesting SES formation. Limited insight could be gained from the 1500–1000 cm^{-1} region (Figure S23a,b) due to the limited spectral intensity and subtle spectral differences in this area; however, similar trends emerged to the H-SAPO-5 with ethanol feedstock. The 4000–3200 cm^{-1} region simply showed a reemergence of the acid site signals (Figure S23c). Our previous calculations suggest that not only is diethyl ether more stable in the H-SAPO-5 pore compared to ethanol (ΔG of -28 and -14 kJ mol^{-1} at 200 °C, respectively) but also that it is slower to diffuse out of the framework.²² This is in good agreement with weakly bound diethyl ether remaining in the system according to the DRIFTS spectra, compared to ethanol. Unlike with the ethanol feedstock, the mass spectrometer showed that using diethyl ether as a feedstock, the ethylene formation occurred at 210 °C but stopped after 300 °C, potentially due to the ether being consumed (Figure S23d), whereas with the ethanol feedstock, ethylene formation continued beyond 300 °C (Figure S23e). This enhanced ethylene formation is again in good agreement with our previous calculations, which suggest a noticeably lower energy barrier to forming ethylene from diethyl ether, compared to ethanol. Overall, by probing both ethanol and diethyl ether feedstocks for ethylene formation, with H-SAPO-5 and H-SAPO-34, we have shown the importance of the surface ethoxy species and shown the influence of diethyl ether as an intermediate (Figure 8).

CONCLUSIONS

Through a combined *in situ* INS, *operando* DRIFTS, and DFT study, we have acquired further evidence to support our proposed catalytic mechanism for ethanol dehydration, with specific emphasis on the importance of the surface ethoxy species and the role of diethyl ether. Comparing the activity of different zeolite frameworks is inherently challenging, due to the difficulty in isolating confinement and acidity influences. Using INS, we demonstrated that H-SAPO-34 readily formed a strongly bound surface ethoxy species above 100 °C, which persevered at high temperatures, in part due to its stability but also due to the difficulties in molecules leaving the large catalyst bed. H-SAPO-5 similarly can form strongly bound ethanol species; however, this combined with its ability to retain some weakly bound ethanol, and its less constrained framework leads to product formation and diffusion out of the system. Our

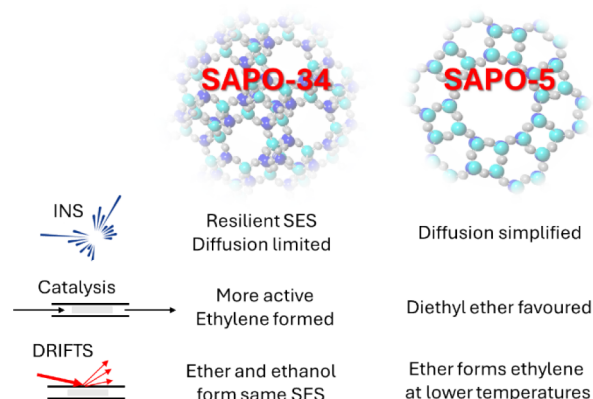


Figure 8. Comparing insights from combined catalysis and characterisation studies on ethanol dehydration.

assignments were guided by DFT-calculated spectra, allowing us to confirm the formation of the SES species. Using *operando* DRIFTS at very high GHSV, we were able to focus on the formation of SES species, again guided by DFT calculations. Here, we saw that in H-SAPO-34, using diethyl ether, or ethanol, leads to a common intermediate, with a similar behavior, being SES. However, the difference in ethanol and diethyl ether behavior was clear in H-SAPO-5. Between the spectroscopic techniques used, there were notable differences in the temperature at which SES species formed. In DRIFTS, we believe that the SES formed almost instantly, though it was not the only species present, whereas, in INS, the spectra resembled frozen ethanol until the system was exposed to higher temperatures. Likely, these differences arise, not only due to the range of techniques used but also due to the dosing process. For the INS measurements, ethanol was introduced at a constant rate with associated helium flow, whereas the IR spectra were initially saturated with ethanol and then exposed to significantly higher GHSV than the INS. Future studies aimed at combining multiple techniques should aim for greater overlap in dosing, and GHSV, to operate in similar regimes.

In both cases, the characterization studies were performed under *pseudo-flow* conditions, with the reagent being introduced at the beginning of the experiment only, with significantly different GHSV. Performing the INS measurements at low GHSV conditions enables investigation of pore diffusion and mass-transfer effects in the catalytic process, allowing us to focus on the retention of reagent and intermediate species. In contrast, performing the DRIFTS measurements at high GHSV suppresses these influences and allows greater focus on the formation and evolution of reaction intermediates. Together, these complementary approaches provide a more comprehensive understanding of the overall reaction mechanism. Such studies are vital for probing the behavior of specific species, and for developing catalytic insights; however, to perfectly align with the catalytic data, continuous flows of reagent should be considered. Currently, this is challenging for many spectroscopic techniques, as signals from unbound reagent can dominate the spectra, dwarfing the intermediates, requiring higher-resolution measurements. However, developments in *operando* characterization are approaching this. Despite this, studies under “pseudo-flow” provide very valuable information on the catalytic mechanism, particularly when guided with theoretical calculations.

Looking forward, this work provides a clearer framework for disentangling the roles of acidity and confinement in zeolite-catalyzed ethanol dehydration, offering mechanistic principles that can guide the rational design of improved catalysts. Complementing *in situ* spectroscopy with DFT establishes a transferable methodology for identifying and validating key reactive intermediates. Moreover, highlighting the limitations of current *operando* approaches underscores the need for advanced spectroscopic methods capable of true continuous-flow measurements, which will be critical for bridging the gap between mechanistic insight and industrially relevant reaction conditions.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.6c02273>.

Literature catalysis values, experimental details, characterization protocols, DFT-calculated IR signals, physico-chemical characterization data, previous catalytic data, INS spectra, and further DRIFTS data (DOCX)

DFT calculated motion of gas phase diethyl ether (XYZ)

DFT calculated motion of gas phase ethanol (XYZ)

DFT calculated motions of H-SAPO-34 with diethyl ether (XYZ)

DFT calculated motions of H-SAPO-34 with ethanol (XYZ)

DFT calculated motions of H-SAPO-34 with ethyl (SES) (XYZ)

DFT calculated motions of H-SAPO-5 with diethyl ether (XYZ)

DFT calculated motions of H-SAPO-5 with ethanol (XYZ)

DFT calculated motions of H-SAPO-5 with ethyl (SES) (XYZ)

■ AUTHOR INFORMATION

Corresponding Authors

Matthew E. Potter – Institute of Sustainability and Climate Change, Department of Chemistry, University of Bath, Bath BA2 7AY, UK; UK Catalysis Hub, Research Complex at Harwell (RCaH), Harwell, Didcot, Oxfordshire OX11 0FA, UK; [ID orcid.org/0000-0001-9849-3306](https://orcid.org/0000-0001-9849-3306); Email: mep61@bath.ac.uk

Dmitry I. Sharapa – Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen 76344, Germany; [ID orcid.org/0000-0001-9510-9081](https://orcid.org/0000-0001-9510-9081); Email: dmitry.sharapa@kit.edu

Authors

Maciej G. Walerowski – School of Chemistry and Chemical Engineering, University of Southampton, Southampton SO17 1BJ, UK

Hamish Cavaye – ISIS Pulsed Neutron and Muon Facility, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Didcot OX11 0QX, UK; [ID orcid.org/0000-0002-3540-0253](https://orcid.org/0000-0002-3540-0253)

Robert Raja – School of Chemistry and Chemical Engineering, University of Southampton, Southampton SO17 1BJ, UK; [ID orcid.org/0000-0002-4161-7053](https://orcid.org/0000-0002-4161-7053)

Lindsay-Marie Armstrong – School of Engineering, University of Southampton, Southampton SO17 1BJ, UK

Marina Carravetta – School of Chemistry and Chemical Engineering, University of Southampton, Southampton SO17 1BJ, UK

Felix Studt – Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen 76344, Germany; Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Kaiserstr. 12, Karlsruhe 76131, Germany; [ID orcid.org/0000-0001-6841-4232](https://orcid.org/0000-0001-6841-4232)

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acscatal.6c02273>

Author Contributions

The manuscript was written through contributions of all authors, and all authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the University of Southampton and the Southampton Marine and Maritime Institute. This work was performed using resources from the UK Catalysis Hub, which was funded by current EPSRC grants EP/R026939/1 and EP/R026815/1 who are gratefully acknowledged. The University of Bath and its Institute of Sustainability and Climate Change are acknowledged for financial support for Dr. M.E. Potter's Prize Fellowship. The ISIS Neutron and Muon Source is thanked for beamtime access on the TOSCA instrument, under experiment allocation number RB2220187. The authors acknowledge support by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no. INST40/575-1FUGG (JUSTUS2cluster, RVs bw17D011). Support from the Helmholtz Association is also gratefully acknowledged.

REFERENCES

- (1) Cui, X.; Hou, D.; Bing, Q.; Hu, J.; Deng, D. Shaping the future of green methanol. *Chem Catal.* **2025**, *5* (9), 101515.
- (2) Zhang, W.; Wen, C.; Zhang, X.; Chen, L.; Zhang, Q.; Ma, L. A Review of Green Methanol Production: Technologies, Economic Evaluation, and Carbon Emission Analysis. *Energy Fuels* **2025**, *39* (39), 18733–18750.
- (3) Fasihi, M.; Breyer, C. Global production potential of green methanol based on variable renewable electricity. *Energy Environ. Sci.* **2024**, *17* (10), 3503–3522.
- (4) Feng, L.; Guo, J.; Pang, J.; Yin, M.; Zhao, Y.; Wu, P.; Zheng, M. Nonenzymatic ethanol production in sustainable ways. *Green Chem.* **2024**, *26* (15), 8564–8582.
- (5) Jamil, F.; Aslam, M.; Al-Muhtaseb, A. a. H.; Bokhari, A.; Rafiq, S.; Khan, Z.; Inayat, A.; Ahmed, A.; Hossain, S.; Khurram, M. S.; Abu Bakar, M. S. Greener and sustainable production of bioethylene from bioethanol: current status, opportunities and perspectives. *Rev. Chem. Eng.* **2022**, *38* (2), 185–207.
- (6) Etzold, B. J. M.; Hungsberg, M.; Ebrahim-Moghaddam, M.; Herold, F.; Dahmen, N.; Studt, F. Energy Requirements for Sustainable Olefin Production From CO₂ via Electro- or Thermal Catalysis. *Chem. Eng. Technol.* **2025**, *48* (6), e70034.
- (7) Wang, J.; Zhang, G.; Zhu, J.; Zhang, X.; Ding, F.; Zhang, A.; Guo, X.; Song, C. CO₂ Hydrogenation to Methanol over In₂O₃-Based Catalysts: From Mechanism to Catalyst Development. *ACS Catal.* **2021**, *11* (3), 1406–1423.
- (8) Ye, R.; Ma, L.; Mao, J.; Wang, X.; Hong, X.; Gallo, A.; Ma, Y.; Luo, W.; Wang, B.; Zhang, R.; Duyar, M. S.; Jiang, Z.; Liu, J. A Ce-Cu-Zn catalyst with abundant Cu/Zn-O(V)-Ce active sites for CO₂ hydrogenation to methanol. *Nat. Commun.* **2024**, *15* (1), No. 2159.
- (9) Raynes, S. J.; Taylor, R. A. Zinc oxide-modified mordenite as an effective catalyst for the dehydrogenation of (bio)ethanol to acetaldehyde. *Sustainable Energy Fuels* **2021**, *5* (7), 2136–2148.
- (10) Ouayloul, L.; Agirrezabal-Telleria, I.; Sebastien, P.; El Doukkali, M. Trend and Progress in Catalysis for Ethylene Production from Bioethanol Using ZSM-5. *ACS Catal.* **2024**, *14* (23), 17360–17397.
- (11) Ngcobo, M.; Makgwane, P. R.; Mathe, M. K. A minireview on solid acid catalysts for dehydration of bioethanol to renewable ethylene:

An update on catalysts development progress. *Appl. Catal. O: Open* **2024**, *193*, No. 206976.

- (12) Yao, J.; Liu, S.; Chen, G.; Yi, W.; Liu, J. Enhanced bioethanol-to-ethylene performance over nanosized sheet-like M-SAPO-34 (M = Sr and K) catalysts. *Microporous Mesoporous Mater.* **2022**, *338*, 111980.

- (13) Moghaddam, A. H.; Esfandyari, M. Optimization of separation and purification processes in diethyl ether production for improved efficiency and sustainability. *Sci. Rep.* **2025**, *15* (1), No. 27911.

- (14) Autthanit, C.; Likitpiriya, N.; Praserttham, P.; Jongsomjit, B. Development of a New Ternary Al₂O₃-HAP-Pd Catalyst for Diethyl Ether and Ethylene Production Using the Preferential Dehydration of Ethanol. *ACS Omega* **2021**, *6* (30), 19911–19923.

- (15) Arumugam, S.; Koranga, K. S.; Gaur, G.; Kasina, D. P. L. K.; Tathod, A. P.; Viswanadham, N. Upgrading Bioethanol to a High-Energy-Density Sustainable Fuel over a Novel Bimetallic Nanocomposite Catalyst. *ACS Sustainable Chem. Eng.* **2025**, *13* (42), 18289–18301.

- (16) Bisarya, A.; Kathuria, L.; Das, K.; Yasmin, E.; Jasra, R. V.; Dhole, S.; Kumar, A. State-of-the-art advances in homogeneous molecular catalysis for the Guerbet upgrading of bio-ethanol to fuel-grade bio-butanol. *Chem. Commun.* **2025**, *61* (14), 2906–2925.

- (17) Liu, Q.; Lin, J.; Cheng, H.; Wei, L.; Wang, F. Simultaneous co-Photocatalytic CO₂ Reduction and Ethanol Oxidation towards Synergistic Acetaldehyde Synthesis. *Am. Ethanol.* **2023**, *135* (13).

- (18) Shen, W.; Tian, Z.; Zhao, L.; Qian, F. Life Cycle Assessment and Multiobjective Optimization for Steam Cracking Process in Ethylene Plant. *ACS Omega* **2022**, *7* (18), 15507–15517.

- (19) Chen, Y.; Kuo, M. J.; Lobo, R.; Ierapetritou, M. Ethylene production: process design, techno-economic and life-cycle assessments. *Green Chem.* **2024**, *26* (5), 2903–2911.

- (20) Wang, R.; Yang, W.; Xu, Y.; Shu, X.; Wang, Y.; Luo, Y.; Xing, E.; Ouyang, Y.; Zhou, L.; Huang, W.; Bai, Y. Increased Ethylene Production by the Combination Technology of Targeted Catalytic Cracking to Olefins and Dehydration of Bioethanol Reaction. *Ind. Eng. Chem. Res.* **2025**, *64* (16), 8079–8088.

- (21) Pornsetmetakul, P.; Klinyod, S.; Rodaum, C.; Salakhum, S.; Iadrat, P.; Hensen, E. J. M.; Wattanakit, C. Fine-Tuning Texture of Highly Acidic HZSM-5 Zeolite for Efficient Ethanol Dehydration. *ChemCatChem* **2023**, *15* (9), e202201387.

- (22) Potter, M. E.; Amsler, J.; Spiske, L.; Plessow, P. N.; Asare, T.; Carravetta, M.; Raja, R.; Cox, P. A.; Studt, F.; Armstrong, L.-M. Combining Theoretical and Experimental Methods to Probe Confinement within Microporous Solid Acid Catalysts for Alcohol Dehydration. *ACS Catal.* **2023**, *13* (9), 5955–5968.

- (23) Ouayloul, L.; El Doukkali, M.; Jiao, M.; Dumeignil, F.; Agirrezabal-Telleria, I. New mechanistic insights into the role of water in the dehydration of ethanol into ethylene over ZSM-5 catalysts at low temperature. *Green Chem.* **2023**, *25* (9), 3644–3659.

- (24) Grifoni, E.; Piccini, G.; Lercher, J. A.; Glezakou, V. A.; Rousseau, R.; Parrinello, M. Confinement effects and acid strength in zeolites. *Nat. Commun.* **2021**, *12* (1), 2630.

- (25) Li, X.; Ma, S.; Li, H. Zeolite confinement-catalyzed cleavage of C–O/C–C bonds in biomass. *Green Chem.* **2022**, *24* (19), 7243–7280.

- (26) Chai, Y.; Dai, W.; Wu, G.; Guan, N.; Li, L. Confinement in a Zeolite and Zeolite Catalysis. *Acc. Chem. Res.* **2021**, *54* (13), 2894–2904.

- (27) Jayakumari, M. T.; Kanakkampalayam Krishnan, C. Tuning Al sites in Y-zeolite for selective production of γ-valerolactone from levulinic acid. *Appl. Catal., A* **2023**, *663*.

- (28) Rzepka, P.; Huthwelker, T.; Dedeczek, J.; Tabor, E.; Bernauer, M.; Sklenak, S.; Mlekodaj, K.; van Bokhoven, J. A. Aluminum distribution and active site locations in the structures of zeolite ZSM-5 catalysts. *Science* **2025**, *388* (6745), 423–428.

- (29) Batool, S. R.; Sushkevich, V. L.; van Bokhoven, J. A. Factors Affecting the Generation and Catalytic Activity of Extra-Framework Aluminum Lewis Acid Sites in Aluminum-Exchanged Zeolites. *ACS Catal.* **2024**, *14* (2), 678–690.

- (30) Quiroga, E.; García, N.; Cifuentes, B.; Cogua, R.; Becerra, J.; Berenguer, J. M.; Cobo, M. Industrial crude bioethanol dehydration to ethylene: Doping ZSM-5 to enhance selectivity and stability. *J. Environ. Chem. Eng.* **2024**, *12* (1), 111803.
- (31) Spennati, E.; Iturrate, M.; Bogno, S.; Cosso, A.; Millini, R.; Riani, P.; Busca, G.; Garbarino, G. Ethanol conversion to hydrocarbons over Sn-doped H-ZSM-5 zeolite catalysts. *Microporous Mesoporous Mater.* **2024**, *379*, 113284.
- (32) Potter, M. E.; Cholerton, M. E.; Kezina, J.; Bounds, R.; Carravetta, M.; Manzoli, M.; Gianotti, E.; Lefenfeld, M.; Raja, R. Role of Isolated Acid Sites and Influence of Pore Diameter in the Low-Temperature Dehydration of Ethanol. *ACS Catal.* **2014**, *4* (11), 4161–4169.
- (33) Potter, M. E.; Armstrong, L.-M.; Raja, R. Combining catalysis and computational fluid dynamics towards improved process design for ethanol dehydration. *Catal. Sci. Technol.* **2018**, *8* (23), 6163–6172.
- (34) Chowdhury, A. D.; Lucini Paioni, A.; Whiting, G. T.; Fu, D.; Baldus, M.; Weckhuysen, B. M. Unraveling the Homologation Reaction Sequence of the Zeolite-Catalyzed Ethanol-to-Hydrocarbons Process. *Angew. Chem., Int. Ed.* **2019**, *58* (12), 3908–3912.
- (35) Dittmann, D.; Kaya, E.; Dyballa, M. Desilicated ZSM-5 Catalysts: Properties and Ethanol to Aromatics (ETA) Performance. *ChemCatChem* **2023**, *15* (20), e202300716.
- (36) Iadrat, P.; Horii, N.; Atitthep, T.; Wattanakit, C. Effect of Pore Connectivity of Pore-Opened Hierarchical MOR Zeolites on Catalytic Behaviors and Coke Formation in Ethanol Dehydration. *ACS Appl. Mater. Interfaces* **2021**, *13* (7), 8294–8305.
- (37) Rodaun, C.; Kinyod, S.; Nunthakitgason, W.; Chaipornchalerm, P.; Liwatthanakul, N.; Iadrat, P.; Wattanakit, C. Binder-free hierarchical zeolite pellets and monoliths derived from ZSM-5@LDHs composites for bioethanol dehydration to ethylene. *Chem. Commun. (Camb)* **2022**, *58* (69), 9618–9621.
- (38) Wang, B.; Zhou, L.; Rui, P.; Wu, Z.; Zhang, W.; Luo, Y.; Liao, W.; Shu, X. An Al-sol gelation strategy for the synthesis of robust hierarchical SAPO-34 with enhanced ethylene selectivity. *Microporous Mesoporous Mater.* **2022**, *343*, No. 112181.
- (39) Potter, M. E. Down the Microporous Rabbit Hole of Silicoaluminophosphates: Recent Developments on Synthesis, Characterization, and Catalytic Applications. *ACS Catal.* **2020**, *10* (17), 9758–9789.
- (40) Kadam, S. A.; Shamzhy, M. V. IR Operando Study of Ethanol Dehydration over MFI Zeolites: Structure–Activity Relationships. *J. Phys. Chem. C* **2018**, *122* (42), 24055–24067.
- (41) Potter, M. E.; Aswegen, S. V.; Gibson, E. K.; Silverwood, I. P.; Raja, R. Spectroscopic investigation into the design of solid-acid catalysts for the low temperature dehydration of ethanol. *Phys. Chem. Chem. Phys.* **2016**, *18* (26), 17303–17310.
- (42) Iadrat, P.; Yomthong, K.; Rodaun, C.; Pornsetmetakul, P.; Thivasasith, A.; Prasertsab, A.; Fan, X.; Sooknoi, T.; Wattanakit, C. Effects of zeolite frameworks and hierarchical structures on catalytic bioethanol dehydration: In-situ DRIFTS and DFT studies. *Fuel* **2023**, *338*, 127208.
- (43) Kondo, J. N.; Ito, K.; Yoda, E.; Wakabayashi, F.; Domen, K. An ethoxy intermediate in ethanol dehydration on Brønsted acid sites in zeolite. *J. Phys. Chem. B* **2005**, *109* (21), 10969–10972.
- (44) Kim, S.; Robichaud, D. J.; Beckham, G. T.; Paton, R. S.; Nimlos, M. R. Ethanol dehydration in HZSM-5 studied by density functional theory: evidence for a concerted process. *J. Phys. Chem. A* **2015**, *119* (15), 3604–3614.
- (45) Xia, H. Monomolecular Dehydration of Ethanol into Ethylene over H-MOR Studied by Density Functional Theory. *ACS Omega* **2020**, *5* (17), 9707–9713.
- (46) Alexopoulos, K.; John, M.; Van der Borgh, K.; Galvita, V.; Reyniers, M.-F.; Marin, G. B. DFT-based microkinetic modeling of ethanol dehydration in H-ZSM-5. *J. Catal.* **2016**, *339*, 173–185.
- (47) Kumar, D.; Sauer, J.; Airi, A.; Bordiga, S.; Galimberti, D. R. Assignment of IR spectra of ethanol at Brønsted sites of H-ZSM-5 to monomer adsorption using a Fermi resonance model. *Phys. Chem. Chem. Phys.* **2024**, *27* (1), 550–563.
- (48) Costa, R. J.; Castro, E. A. S.; Politi, J. R. S.; Gargano, R.; Martins, J. B. L. Methanol, ethanol, propanol, and butanol adsorption on H-ZSM-5 zeolite: an ONIOM study. *J. Mol. Model.* **2019**, *25* (2), No. 34.
- (49) Piccini, G.; Alessio, M.; Sauer, J. Ab initio study of methanol and ethanol adsorption on Brønsted sites in zeolite H-MFI. *Phys. Chem. Chem. Phys.* **2018**, *20* (30), 19964–19970.
- (50) Hemelsoet, K.; Ghysels, A.; Mores, D.; De Wispelaere, K.; Van Speybroeck, V.; Weckhuysen, B. M.; Waroquier, M. Experimental and theoretical IR study of methanol and ethanol conversion over H-*SAPO-34*. *Catal. Today* **2011**, *177* (1), 12–24.
- (51) Zachariou, A.; Hawkins, A. P.; Collier, P.; Howe, R. F.; Parker, S. F.; Lennon, D. Neutron scattering studies of the methanol-to-hydrocarbons reaction. *Catal. Sci. Technol.* **2023**, *13* (7), 1976–1990.
- (52) Lin, L.; Mei, Q.; Han, X.; Parker, S. F.; Yang, S. Investigations of Hydrocarbon Species on Solid Catalysts by Inelastic Neutron Scattering. *Top. Catal.* **2020**, *64* (9–12), 593–602.
- (53) Jiménez-Ruiz, M.; Lemishko, T.; Rey, F.; Sastre, G. Carbonylation of dimethyl ether in mordenite using Inelastic Neutron Scattering. *Microporous Mesoporous Mater.* **2024**, *364*, 112850.
- (54) Nikolic, M.; Daemen, L.; Ramirez-Cuesta, A. J.; Xicohtencatl, R. B.; Cheng, Y.; Putnam, S. T.; Stadie, N. P.; Liu, X.; Terreni, J.; Borgschulte, A. Neutron Insights into Sorption Enhanced Methanol Catalysis. *Top. Catal.* **2021**, *64* (9–12), 638–643.
- (55) Strange, N. A.; Adak, S.; Stroupe, Z.; Crain, C. A.; Novak, E. C.; Daemen, L. L.; Larese, J. Z. A multi-faceted structural, thermodynamic, and spectroscopic approach for investigating ethanol dehydration over transition phase aluminas. *Phys. Chem. Chem. Phys.* **2022**, *25* (1), 590–603.
- (56) Bowden, Z. A.; Celli, M.; Cilloco, F.; Colognesi, D.; Newport, R. J.; Parker, S. F.; Ricci, F. P.; Rossi-Albertini, V.; Sacchetti, F.; Tomkinson, J.; Zoppi, M. The TOSCA incoherent inelastic neutron spectrometer: progress and results. *Phys. B* **2000**, 276–278, 98–99.
- (57) Pinna, R. S.; Rudić, S.; Parker, S. F.; Armstrong, J.; Zanetti, M.; Škoro, G.; Waller, S. P.; Zacek, D.; Smith, C. A.; Capstick, M. J.; McPhail, D. J.; Pooley, D. E.; Howells, G. D.; Gorini, G.; Fernandez-Alonso, F. The neutron guide upgrade of the TOSCA spectrometer. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2018**, *896*, 68–74.
- (58) Yu, X.; Cheng, Y.; Li, Y.; Polo-Garzon, F.; Liu, J.; Mamontov, E.; Li, M.; Lennon, D.; Parker, S. F.; Ramirez-Cuesta, A. J.; Wu, Z. Neutron Scattering Studies of Heterogeneous Catalysis. *Chem. Rev.* **2023**, *123* (13), 8638–8700.
- (59) Armstrong, J.; Rudic, S. TOSCA. *ISIS Neutron and Muon Source* **2026**.
- (60) Potter, M. Exploring the formation of ethoxy species in microporous solid-acid catalysts. *ISIS Neutron Muon Source* **2022**.
- (61) Warringham, R.; Bellaire, D.; Parker, S. F.; Taylor, J.; Ewings, R. A.; Goodway, C. M.; Kibble, M.; Wakefield, S. R.; Jura, M.; Dudman, M. P.; Tooze, R. P.; Webb, P. B.; Lennon, D. Sample environment issues relevant to the acquisition of inelastic neutron scattering measurements of heterogeneous catalyst samples. *J. Phys.:Conf. Ser.* **2014**, *554*, No. 012005.
- (62) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter* **1996**, *54* (16), 11169–11186.
- (63) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6* (1), 15–50.
- (64) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.
- (65) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys. Rev. Lett.* **1997**, *78* (7), 1396–1396.
- (66) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), No. 154104.

(67) Vicente, H.; Plessow, P. N. Formaldehyde formation and its impact on the MTO initiation investigated with ab initio molecular dynamics simulations. *J. Catal.* **2026**, *457*, 116817.

(68) Van Speybroeck, V.; Bocus, M.; Cnudde, P.; Vanduyffhuys, L. Operando Modeling of Zeolite-Catalyzed Reactions Using First-Principles Molecular Dynamics Simulations. *ACS Catal.* **2023**, *13* (17), 11455–11493.

(69) Mantid Project Mantid 6.12.0; **2025**. <http://dx.doi.org/10.5286/SOFTWARE/MANTID6.12>.

(70) Arnold, O.; Bilheux, J. C.; Borreguero, J. M.; Buts, A.; Campbell, S. I.; Chapon, L.; Doucet, M.; Draper, N.; Ferraz Leal, R.; Gigg, M. A.; Lynch, V. E.; Markvardsen, A.; Mikkelsen, D. J.; Mikkelsen, R. L.; Miller, R.; Palmen, K.; Parker, P.; Passos, G.; Perring, T. G.; Peterson, P. F.; Ren, S.; Reuter, M. A.; Savici, A. T.; Taylor, J. W.; Taylor, R. J.; Tolchenov, R.; Zhou, W.; Zikovsky, J. Mantid—Data analysis and visualization package for neutron scattering and μ SR experiments. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2014**, *764*, 156–166.

(71) Dymkowski, K.; Parker, S. F.; Fernandez-Alonso, F.; Mukhopadhyay, S. AbINS: The modern software for INS interpretation. *Phys. B* **2018**, *551*, 443–448.

(72) Hjorth Larsen, A.; Jorgen Mortensen, J.; Blomqvist, J.; Castelli, I. E.; Christensen, R.; Dulak, M.; Friis, J.; Groves, M. N.; Hammer, B.; Hargus, C.; Hermes, E. D.; Jennings, P. C.; Bjerre Jensen, P.; Kermode, J.; Kitchin, J. R.; Leonhard Kolsbjerg, E.; Kubal, J.; Kaasbjerg, K.; Lysgaard, S.; Bergmann Maronsson, J.; Maxson, T.; Olsen, T.; Pastewka, L.; Peterson, A.; Rostgaard, C.; Schiotz, J.; Schutt, O.; Strange, M.; Thygesen, K. S.; Vegge, T.; Vilhelmsen, L.; Walter, M.; Zeng, Z.; Jacobsen, K. W. The atomic simulation environment—a Python library for working with atoms. *J. Phys.: Condens. Matter* **2017**, *29* (27), 273002.

(73) Sastre, G.; Lewis, D. W.; Catlow, C. R. A. Modeling of Silicon Substitution in SAPO-5 and SAPO-34 Molecular Sieves. *J. Phys. Chem. B* **1997**, *101* (27), S249–S262.

(74) Parker, S. F. Ethanol(2017) STFC eData Repository.

(75) Aldiyarov, A.; Aryutkina, M.; Drobyshchev, A.; Kaikanov, M.; Kurnosov, V. Investigation of dynamic glass transitions and structural transformations in cryovacuum condensates of ethanol. *Low Temp. Phys.* **2009**, *35* (4), 251–255.

(76) Durig, J. R.; Larsen, R. A. Torsional vibrations and barriers to internal rotation for ethanol and 2,2,2-trifluoroethanol. *J. Mol. Struct.* **1990**, *238*, 195–222.

(77) Golay, S.; Doepper, R.; Renken, A. In-situ characterisation of the surface intermediates for the ethanol dehydration reaction over γ -alumina under dynamic conditions. *Appl. Catal., A* **1998**, *172* (1), 97–106.

(78) Corsaro, C.; Crupi, V.; Majolino, D.; Parker, S. F.; Venuti, V.; Wanderlingh, U. Inelastic neutron scattering study of water in hydrated LTA-type zeolites. *J. Phys. Chem. A* **2006**, *110* (3), 1190–1195.

(79) Hall, P. G.; Pidduck, A.; Wright, C. J. Inelastic neutron scattering by water adsorbed on silica. *J. Colloid Interface Sci.* **1981**, *79* (2), 339–349.

(80) Matam, S. K.; Howe, R. F.; Thetford, A.; Catlow, C. R. A. Room temperature methoxylation in zeolite H-ZSM-5: an operando DRIFTS/mass spectrometric study. *Chem. Commun.* **2018**, *54* (91), 12875–12878.

(81) Phung, T. K.; Busca, G. Diethyl ether cracking and ethanol dehydration: Acid catalysis and reaction paths. *Chem. Eng. J.* **2015**, *272*, 92–101.

(82) Sousa, Z. S. B.; Cesar, D. V.; Henriques, C. A.; Teixeira da Silva, V. Bioethanol conversion into hydrocarbons on HZSM-5 and HMCM-22 zeolites: Use of in situ DRIFTS to elucidate the role of the acidity and of the pore structure over the coke formation and product distribution. *Catal. Today* **2014**, *234*, 182–191.

(83) Zachariou, A.; Hawkins, A. P.; Howe, R. F.; Barrow, N.; Bradley, J.; Collier, P.; Lennon, D.; Parker, S. F. A Spectroscopic Paradox: The Interaction of Methanol with ZSM-5 at Room Temperature. *Top. Catal.* **2021**, *64* (9–12), 672–684.