

# Onset of Propene Oligomerization Reactivity in ZSM-5 Studied by Inelastic Neutron Scattering Spectroscopy

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Cite This: *ACS Omega* 2020, 5, 7762–7770



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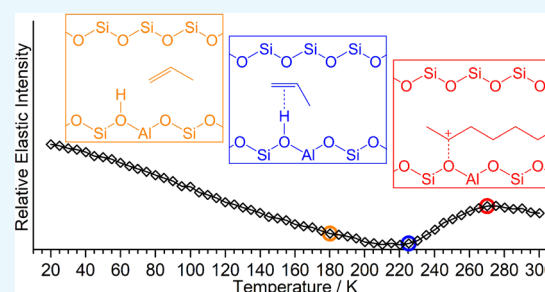


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**ABSTRACT:** The techniques of quasi-elastic and inelastic neutron scattering (QENS and INS) are applied to investigate the oligomerization of propene over a ZSM-5 zeolite. Investigations are performed at low temperatures, allowing identification of the onset of the oligomerization reaction and observation of the low-energy spectral changes due to intermediate formation that are difficult to observe by optical methods. Oligomerization proceeds via formation of a hydrogen-bonded precursor by an interaction of the propene with an internal acid site followed by protonation and chain growth with protonation being the rate-limiting step. The use of quasi-elastic neutron scattering to observe changes in system mobility with temperature via the elastic window scan technique allows identification of the active temperature range where catalyst activity commences and permits targeting of the more time-consuming INS investigations to conditions of interest. From examination of the product's spectrum, the structure of the resulting oligomer is deduced to be primarily linear.



## INTRODUCTION

The solid acid oligomerization of small olefin molecules by protonated zeolite catalysts offers an effective industrial strategy for the generation of C–C bonds and production of larger hydrocarbon molecules.<sup>1–5</sup> As such it provides a route to the valorisation of light hydrocarbons from nonfuel fractions in the petrochemical industry and for upgrading biomass-derived oxygenates through the use of olefins as an intermediate.<sup>4</sup> In addition to these potential direct applications, acid oligomerization is also a contributory reaction in several chemical processes, which are important to the petrochemical industry. It contributes to the formation and evolution of the “hydrocarbon pool” in the methanol-to-hydrocarbon series of reactions,<sup>6–8</sup> and, as the inverse reaction to the  $\beta$ -scission mechanism by which alkenes are cracked in commercial fluidized catalytic cracking (FCC) reactors, it is therefore an important contributor to the final FCC product stream.<sup>9</sup> In all of these processes, oligomerization reactions occur in an equilibrium with isomerization and  $\beta$ -scission reactions of the oligomerized product with the final product composition being determined by reaction conditions and steric effects from the zeolite pores. Generally, oligomerization and isomerization reactions predominate at low temperatures, while cracking reactions are reported to require temperatures higher than 693 K to make significant contributions to the equilibrium,<sup>10,11</sup> Indeed, isomerizations are reported to occur at temperatures as low as 293 K.<sup>12–14</sup> A full understanding of the mechanisms of olefin oligomerization over zeolites is therefore important to

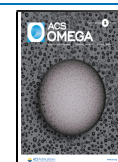
both improving reactions key to efficient utilization of petrochemical reserves by conversion of both short- and long-chain-length low-demand fractions and the development of non-fossil-fuel routes to petrochemical derivatives.

Neutron scattering techniques offer the possibility of new insights into the interaction of hydrocarbons with zeolite catalysts through enabling a clearer observation of low-energy regions of the vibrational energy spectrum. The exceptionally high inelastic incoherent scattering cross section of hydrogen means that the spectra obtained by inelastic neutron scattering (INS) spectrometers are dominated by the hydrocarbon contributions and the zeolite lattice modes, which otherwise dominate the infrared spectrum at energies below 1600  $\text{cm}^{-1}$ , do not significantly contribute. This allows access to the deformation region of the hydrocarbon spectrum without interferences, providing easier identification of intermediate hydrocarbon species. The further ability of quasi-elastic neutron scattering (QENS) to observe energy changes corresponding to molecular rotations and translations also offers the ability to quantify hydrocarbon mobility changes due to oligomerization. The time and length scales accessible by

Received: October 20, 2019

Accepted: February 20, 2020

Published: March 30, 2020



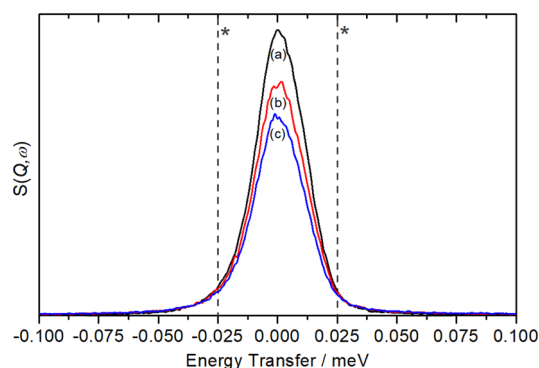
QENS closely match those associated with confined hydrocarbon diffusion in zeolites,<sup>15</sup> and they have been previously used to identify transition temperatures associated with such factors as antifreeze effects in water–sugar mixtures.<sup>16</sup>

We have previously utilized these advantages to study (i) the linear product of the oligomerization of 1-octene in ZSM-5<sup>13</sup> and, in a preliminary study, (ii) the oligomerization of propene within ZSM-5.<sup>14</sup> The latter study proposed a linear reaction mechanism for the oligomerization and showed that it was possible to adsorb the propene into the ZSM-5 pore structure without triggering oligomerization provided that propene loading was performed at sufficiently low temperatures.<sup>14</sup> This scenario offers the possibility of observing the oligomerization reaction in progress by loading the propene below its reaction temperature and subsequently observing the reaction by neutron methods as it occurs *in situ*. This paper reports the use of INS and QENS techniques to observe the oligomerization reaction of propene in progress and the direct observation of intermediate species. Thus, this heightened awareness of light olefin interactions over ZSM-5 connects with contemporary hydrocarbon refining practices.

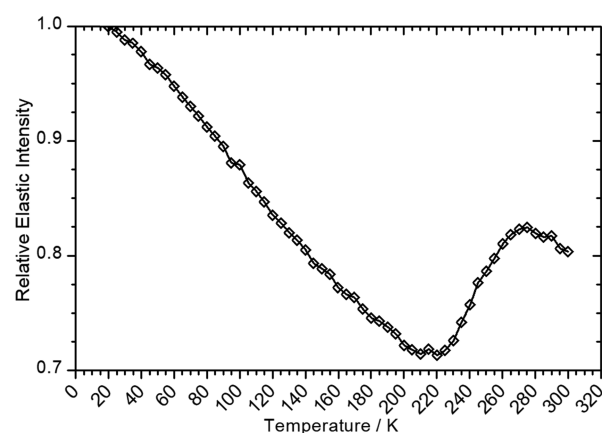
## RESULTS AND DISCUSSION

Previous studies of the interactions of propene in ZSM-5 have shown that the adsorbed propene undergoes rapid oligomerization to generate long-chain alkane species at temperatures as low as 293 K, while this reaction does not occur at cryogenic temperatures.<sup>14</sup> Since this reaction involves the formation of larger molecules, it results in a reduction in the overall mobility of the ZSM-5/hydrocarbon system since the large oligomer molecules are not able to diffuse freely through the zeolite pores. It is therefore possible to quantify the progression of the reaction with temperature by means of quasi-elastic neutron scattering (QENS), which provides information on the motions of molecules with the degree of mobility determining the extent of broadening of the QENS peak.<sup>17</sup> Summing the collected neutron scattering intensity across the full range of scattering angles ( $Q$ ) and integrating the resulting peak across an energy transfer range of  $\pm 25 \mu\text{eV}$  produces an estimate of the elastic intensity at each temperature. Normalizing these values against the value recorded at the base temperature produces a plot of relative elastic intensity against temperature, referred to as an “elastic window scan”. Since elastic intensity embodies the contributions of the immobile proportion of the sample only, it follows that the value of this plot is inversely proportional to overall sample mobility. As the sample temperature increases, the relative elastic intensity will decrease as the propene molecules become more mobile, as shown in Figure 1. The oligomerization reaction will reverse this trend as the small propene molecules are converted to less mobile long-chain species. Once the oligomerization has run to completion, the downward trend in elastic intensity with temperature will resume as the final product mixture moves more with increased thermal energy. Due to utilizing the sum of the elastic intensity across all  $Q$  values, a spectrum suitable for generating an elastic window scan data point can be collected in a much shorter time period than required for an INS spectrum.

An elastic window scan for the propene/ZSM-5 system from 20 to 300 K is presented in Figure 2 and shows the expected elastic intensity profile, allowing the identification of the minimum temperature for the oligomerization reaction to occur being at 225 K. The decrease in mobility due to



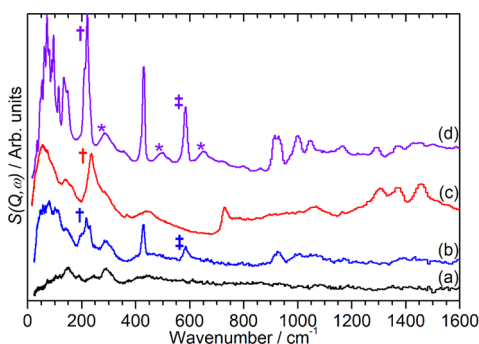
**Figure 1.** Quasielastic scattering functions for propene in ZSM-5 at (a) 20, (b) 120, and (c) 220 K showing increasing temperature leading to decreased intensity within the bounds of the elastic scattering energy transfer range, defined by the resolution limit of OSIRIS (\*), indicative of higher sample mobility.



**Figure 2.** Relative elastic intensity vs temperature for propene in ZSM-5 from 20 to 300 K. Intensity values normalized against  $T = 20$  K.

oligomerization is not instantaneous but occurs over a range of temperatures from 225 to 270 K in contrast to rapid oligomerization, which was noted to occur when the loading took place above this range. This indicates that the reaction is only partially complete in this range of temperatures and defines the temperature range of interest for the more detailed investigation by INS, which was carried out on TOSCA.

With the temperature range where oligomerization begins identified by means of the QENS data, the INS spectra collected across this region allows more detailed investigation of the oligomerization reaction mechanism. Figure 3 shows the start (140 K, (b)) and end (293 K, (c)) state spectra of the sample compared to reference spectra of the empty zeolite and pure propene. The 140 K spectrum shows all the modes that are observed in the spectrum of pure propene, confirming that the adsorbed propene has not reacted when introduced at this temperature. The major difference observed is the splitting of the  $=\text{C}-\text{CH}_3$  torsion mode from a single peak at  $221 \text{ cm}^{-1}$  to a complex feature with peaks at 200, 216, and  $230 \text{ cm}^{-1}$ . From the three peaks in the 140 K spectrum, we can deduce that the propene is present in multiple environments in this sample, potentially representing internally and externally adsorbed propene. Above  $250 \text{ cm}^{-1}$  differences between the free and 140 K adsorbed propene spectra are minor, consisting of some broadening of the peaks, potentially due to propene–zeolite



**Figure 3.** INS spectra of propene adsorbed in ZSM-5 at (b) 140 and (c) 293 K compared to reference spectra of (d) pure propene and (a) the unloaded zeolite. Spectra recorded on TOSCA, scaled to the quantity of propene in each sample and offset in the y axis for clarity. Marked peaks: (†) = methyl torsion, (‡) = vinyl torsion, and (\*) = phonon wing modes.

interactions, a higher level of background intensity due to the essentially flat contribution of the zeolite in the 400–2000  $\text{cm}^{-1}$  region, and suppression of the phonon wing (combinations between internal modes and the external density of states) modes, which are visible at 287, 496, and 652  $\text{cm}^{-1}$  in the pure propene spectrum. The assignment of the modes in the propene and 140 K spectra is given in Table 1 and

**Table 1. Peak Assignments for the TOSCA INS Spectrum of Propene Shown in Figure 3 and the Corresponding Peaks in the Combined 140 K ZSM-5 + Propene Spectrum (Assignments Based on Previously Reported Investigations of Propene<sup>14,18,19</sup>)**

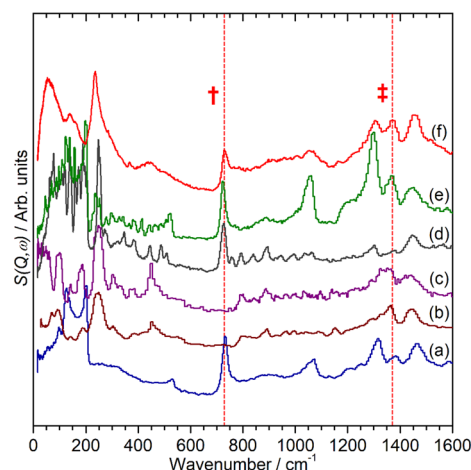
wavenumber ( $\text{cm}^{-1}$ )	assignment
221	—CH <sub>3</sub> torsion
287	wing mode of the 221 $\text{cm}^{-1}$ peak
429	C=C—C scissors
496	wing mode of the 429 $\text{cm}^{-1}$ peak
584	C=CH <sub>2</sub> torsion
652	wing mode of the 584 $\text{cm}^{-1}$ peak
915	C=CH <sub>2</sub> out-of-plane rock
929	C=CH <sub>2</sub> out-of-plane rock
1002	C—H out-of-plane rock
1048	—CH <sub>3</sub> out-of-plane rock
1169	—CH <sub>3</sub> in-plane rock
1291	C—H in-plane rock
1371	—CH <sub>3</sub> symmetric deformation
1440	=CH <sub>2</sub> scissors
1500	—CH <sub>3</sub> asymmetric deformation

corresponds to the results previously reported.<sup>14</sup> In addition to the methyl torsion, modes of particular importance are the vinyl scissors mode at 429  $\text{cm}^{-1}$  and vinyl torsion at 584  $\text{cm}^{-1}$ .

The spectrum of the sample adsorbed at 293 K shows clear evidence of the oligomerization reaction with the absence of any vinyl modes indicating that the reaction has proceeded to completion at this temperature, as predicted by the QENS results (Figure 2). Examination of the infrared spectrum of the ZSM-5/propene system, available as Figure S1 in the Supporting Information to this paper, confirms this with the reduction in the intensity of the zeolite  $\nu(\text{O—H})$  mode at 3610  $\text{cm}^{-1}$  indicating the consumption of Brønsted acid sites, while the fact that all  $\nu(\text{C—H})$  modes are located below 3000  $\text{cm}^{-1}$

indicates that the oligomer is fully saturated. An interference from the zeolite framework bands means that no hydrocarbon modes below 2700  $\text{cm}^{-1}$  are resolvable in the infrared spectrum even if the zeolite contributions are subtracted from the loaded spectrum, meaning that direct comparison of infrared data with the modes detected by INS is not possible.

Studies of the room-temperature oligomerization of propene over ZSM-5 in the literature generally report the product oligomer being a zeolite-bonded alkoxide molecule with one methyl side chain per incorporated propene molecule, analogous to atactic polypropene.<sup>5,12</sup> The production of more linear alkoxides in the C<sub>12</sub> length range is also reported.<sup>19</sup> However, neither of these possibilities provides a good match for the end-state oligomer spectrum in this case. As shown in Figure 4, comparison of the 293 K reacted sample with



**Figure 4.** INS spectrum of propene adsorbed in ZSM-5 at 293 K (f) compared to possible oligomer reference spectra sourced from the ISIS INS database: (a) polyethylene, (b) atactic polypropylene, (c) isotactic polypropylene, (d) C<sub>12</sub>H<sub>26</sub>, and (e) C<sub>44</sub>H<sub>90</sub>.<sup>25</sup> All spectra are recorded on TOSCA. The locations of the CH<sub>2</sub> in-phase rock (†) and CH<sub>2</sub> wag (‡) modes in the adsorbed spectrum are highlighted.

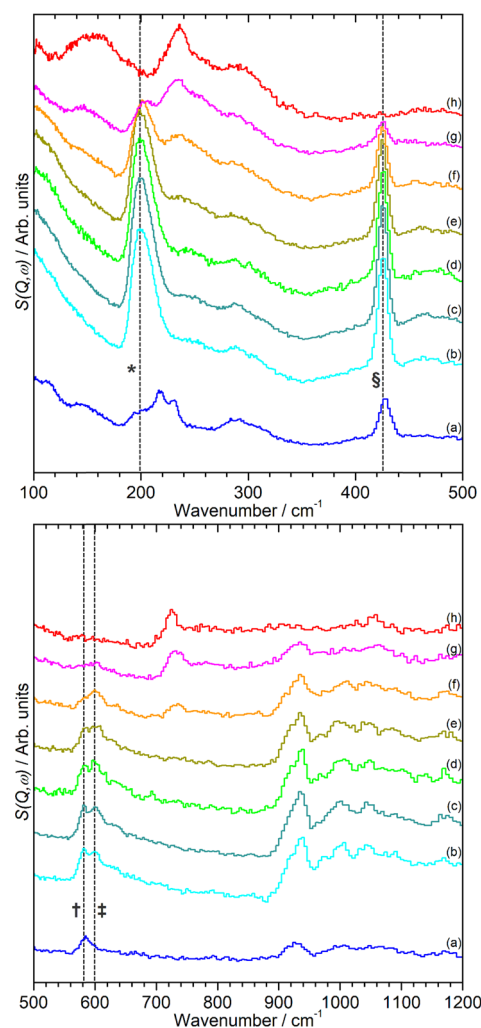
experimental reference spectra of various polypropene tacticities provides a poor match due to the reference spectra's limited number of methylene modes, while dodecane exhibits insufficient peak broadening and low intensity of the CH<sub>2</sub> wag mode located at 1370  $\text{cm}^{-1}$ . The ZSM-5/propene 293 K experimental spectrum also lacks modes that can be attributed to —CH— groups or side chains. The spectra of polyethylene and long-chain alkanes (of which C<sub>44</sub>H<sub>90</sub> is included as a representative sample) provide a much closer match, indicating that the oligomerization reaction has been limited to a linear end-to-end mechanism by the zeolite pore structure, resulting in a primarily linear product mixture. Our previous studies into propene oligomerization have attributed the predominance of linear oligomers to the majority of reactions occurring at interior acid sites<sup>14</sup> with the side branches being incorporated into the chain backbone prior to further oligomerization of the adsorbed alkoxide. Such primarily linear products have previously been observed using NMR by van den Berg and co-workers at 300 K<sup>20</sup> and by Chen and Bridger at higher temperatures up to 503 K in ZSM-5 samples where the surface acid sites have been selectively deactivated;<sup>21</sup> they propose a 1,2-hydride shift mechanism, which positions the cationic charge adjacent to the methyl branch, allowing its incorporation into the chain backbone through a protonated



cyclopropyl intermediate with both reactions being driven by the greater heat of adsorption of linear chains in the ZSM-5 pores. Hydride shifts of this form are known to contribute to the rearrangement of long aliphatic carbocations,<sup>22</sup> and this process is felt to provide an indirect explanation for the linearization of the oligomer shown by the experimental data (Figure 4). It is interesting to note that the highest temperatures where linear oligomerization has been observed are greater than the temperature found to generate primarily branched oligomers in the infrared investigations of Spoto et al.,<sup>12</sup> indicating that the geometry of the final oligomers is not simply a low-temperature effect but may be related to, among other things, differences in the zeolite crystallite size.<sup>14</sup> Relative peak heights in the experimental oligomer spectrum do not precisely match those found in any of the reference linear alkanes; thus, the final product mixture likely consists of a mixture of alkoxide species with multiple chain lengths. Modes that are present in both the adsorbed propene spectrum and linear reference spectra exhibit an  $\sim 5$   $\text{cm}^{-1}$  shift to higher energies, which is attributed to the fact that the reference compounds were recorded as bulk solid samples.

The sequential heating of the sample loaded at 140 K to temperatures in the 200–273 K region provides further information on the mechanism by which the oligomerization reaction progresses. Regions of interest in the INS spectra of the sample recorded after heating to each temperature are shown in Figure 5; the full INS spectrum from 0 to 1600  $\text{cm}^{-1}$  is available as Figure S2 in the Supporting Information. The high resolution of TOSCA allows the observation of small changes in the spectra due to intermediate formation. After heating the sample to 200 K, some changes are visible despite the QENS data suggesting that this temperature lies below the point at which significant changes in sample mobility start to occur. The most notable change is the splitting of the 585  $\text{cm}^{-1}$  peak, corresponding to the twisting motion of the propene C=C bond into a pair of peaks at 581 and 600  $\text{cm}^{-1}$ . This is attributed to the formation of an intermediate consisting of a propene hydrogen-bonded to a Brønsted acid site with this intermediate being responsible for the higher energy peak in the doublet and the remaining physisorbed propene being responsible for the 581  $\text{cm}^{-1}$  signal. The formation of such hydrogen-bonded intermediates as the first step in the oligomerization reactions of light olefins over acid zeolites is reported in the literature.<sup>12,24–26</sup> Although the H-bonded transition states are only observed experimentally in these reactions at low temperatures, this is regarded as a spectroscopic limitation due to their transient nature at higher temperatures. Computational studies confirm that H-bonded  $\pi$  complexes remain a necessary first intermediate in the oligomerization reaction mechanism at temperatures closer to industrial conditions.<sup>27</sup>

An increase in the overall spectral intensity relative to the spectrum at 140 K is also observed, consistent with an increase in the amount of hydrogen nuclei in the neutron beam. Since the sample cell at this point in the experiment is a closed system, the most likely source of the additional hydrogens is from the adsorption of propene previously located in the headspace of the sample cell into the zeolite. No further intensity increases relative to the 200 K spectrum are observed for the following temperature points indicating that all the propene is adsorbed at 200 K and above. Further evidence for this is provided by the shift of all the methyl torsion intensity into the peak at 200  $\text{cm}^{-1}$ , indicating that all the propene



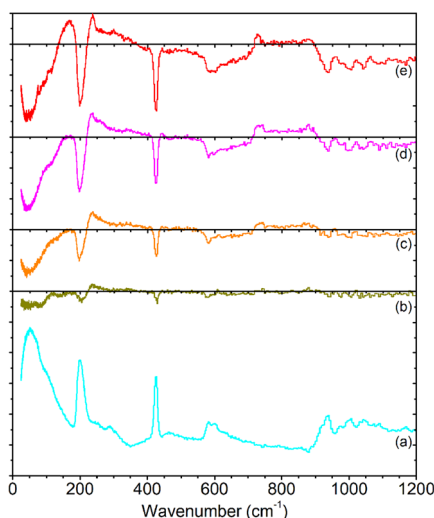
**Figure 5.** Selected regions of the TOSCA INS spectra of propene after absorption into ZSM-5 at (a) 140 K then following further heating to the indicated temperatures: (b) 200 K, (c) 215 K, (d) 225 K, (e) 240 K, (f) 255 K, (g) 270 K, and (h) 293 K. Spectra are offset in the y axis for clarity. The positions of (\*) the methyl torsion, (§) vinyl scissors, and (†, ‡) unbonded and bonded vinyl torsions in the 200 K spectrum are highlighted.

present is now in the same external environment and the 200  $\text{cm}^{-1}$  peak in the 140 K spectrum represents the fraction of the propene that is within the zeolite pore network at that temperature. Since neither the methyl torsion nor the vinyl=CH<sub>2</sub> scissors modes are split in the same fashion as that of the C=C torsion, the hydrogen bonding in the intermediate does not appear to be strong enough to affect modes that do not involve the C=C bond itself.

Further heating to 215 and 225 K does not result in significant changes, although some transfer of intensity occurs between the 581 and 600  $\text{cm}^{-1}$  peaks, indicating a slight increase in the proportion of hydrogen-bonded propene and confirming this entity to be the intermediate responsible for the higher energy peak. Reaching 240 K results in new changes, namely, a reduction in the intensity of peaks associated with the vinyl group, most clearly observable with the vinyl scissors mode at 430  $\text{cm}^{-1}$ , and the shifting of some of the intensity in the methyl torsion peak to a higher value (235  $\text{cm}^{-1}$ ) consistent with the change in internal effects on the transition energy from being part of a longer chain length. At 255 K, a

broad oligomer longitudinal acoustic mode (LAM) becomes visible above the level of background noise at  $155\text{ cm}^{-1}$ .

Figure 6 presents INS difference spectra obtained by subtracting the spectrum obtained after treatment at 200 K

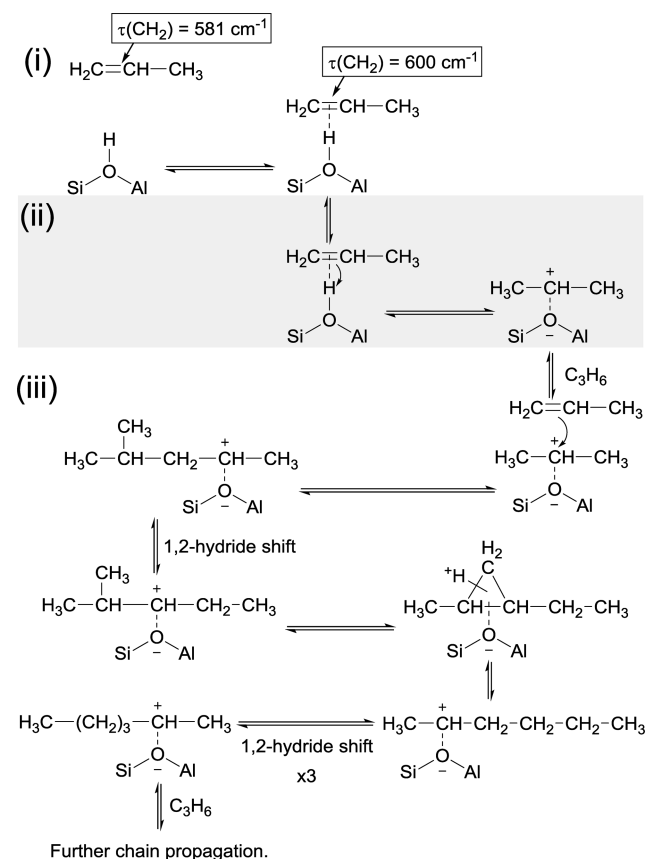


**Figure 6.** Difference plots of selected spectra from Figure 5 relative to the spectrum at (a) 200 K; (b) 240 K, (c) 255 K, (d) 270 K, and (e) = 293 K. All spectra are reproduced at the same scale.

from the 240–293 K datasets that renders these changes more apparent. The spectra indicate the initiation of a further reaction step, which consumes the C=C bond and confirms that the oligomerization reaction begins at 240 K, as indicated by the QENS results. Continued heating results in a decrease of vinyl mode intensity. The growth of peaks in the methylene region of the spectrum is also apparent, which are clearly visible in the difference spectra from 255 K upward until the final spectrum is achieved at 293 K. Some propene molecules remain to contribute to the spectrum at temperatures as high as 270 K, although at this temperature, the  $581\text{ cm}^{-1}$  vinyl peak has been completely suppressed, so the propene is purely present in the hydrogen-bonded intermediate form.

Taken together, these results can be interpreted as signifying that the oligomerization reaction proceeds via a three-step mechanism as illustrated in Scheme 1: (i) initial formation of an olefin hydrogen-bonded to an acid site as an intermediate (as signified by the C=CH<sub>2</sub> torsion at  $600\text{ cm}^{-1}$ ) followed by (ii) protonation of the bonded olefin to form a carbocation and (iii) subsequent oligomerization through the hydride-shift mechanism previously discussed to give a primarily linear product. This is in agreement with previous studies into olefin oligomerization over zeolites,<sup>20,21</sup> while the large temperature range from 200 to 240 K where the hydrogen-bonded intermediate is stable is consistent with the report that it is the olefin protonation that forms the rate-limiting step in olefin oligomerizations.<sup>9,12</sup> Although step ii of the reaction is observed to commence at a temperature close to the boiling point of free propene (225 K), this is believed to be a coincidence; other studies of low-temperature propene oligomerization over H-mordenite report temperatures for the initiation of this phase of the reaction, which are lower by over 40 K, indicating that oligomerization can take place well below the free propene boiling point.<sup>24</sup> Examination of the shape of the positive peaks in the difference spectra indicates that the reacted oligomers exhibit the broadened shape

### Scheme 1. Three-Step Mechanism for Oligomerization of Propene over H-ZSM-5 (Adapted from Ref 19)



characteristic of the final long-chain alkane product mixture (e.g., Figure 3c) even at the lowest temperature where a reaction occurs (Figure 6b,c). Combined with the continued presence of propene molecules up to 270 K, it can be deduced that the propene oligomerization reaction is extremely slow at temperatures below 270 K but the reaction proceeds to yield alkoide oligomers in the same range of final chain lengths regardless of temperature.

This hypothesis is consistent with the fact that kinetic studies of alkene oligomerization report carbocation chain length as not having a noticeable effect on the activation energy required for the further addition of an additional alkene onto the carbocation chain.<sup>9</sup> The system being in an equilibrium that shifts with increasing temperature is not a suitable explanation since  $\beta$ -scission reactions are universally reported to become more significant with increasing temperature, which would result in a decrease in average chain length.<sup>4,12</sup> Systems where  $\beta$  scission is a significant contributor are also reported to result in a product stream, which is primarily olefinic in character at temperatures lower than 500 K.<sup>26</sup> Since neither of these observations is the case for this system, it can be concluded that, for this catalyst, cracking reactions do not make a significant contribution in the temperature range investigated and the intermediate character of the hydrocarbon–zeolite system in the 225–270 K temperature range is purely due to slow kinetics of the oligomerization reaction at these temperatures. Since the length of the oligomer chains is not temperature-dependent, it is most likely determined by steric effects from the zeolite pores. As previously noted, from the fact that the ratio of peak

heights in the final spectrum does not exactly match any available model compound spectrum for linear alkanes, it can be concluded that multiple alkoxide chain lengths are present. While it is possible to obtain an estimate of the average straight chain length in bulk or aqueous linear oligomers from the energy of the longitudinal acoustic mode peak,<sup>28–30</sup> the unknown nature of the effect zeolite–oligomer interactions has on the positioning of the LAM precludes the application of this technique in this case.

## CONCLUSIONS

These results indicate that propene oligomerization in ZSM-5 zeolites can occur at temperatures as low as 225 K, although oligomer formation only becomes large enough to significantly impact the INS spectrum at temperatures of 240 K and above; preliminary hydrogen bonding of adsorbed propene can occur down to ca. 200 K. Below this temperature the liquid propene is adsorbed into the zeolite without undergoing chemical changes. At temperatures high enough to initiate a reaction, the oligomerization reaction requires the formation of a hydrogen-bonded olefin-acid intermediate as a first step, and it then proceeds via protonation of the bonded olefin to form a carbocation and subsequent C–C bond formation with further propene molecules, which are free in the zeolite pores. The protonation of the H-bonded propene is thought to be the rate-limiting step, and once a carbocation is formed, subsequent chain growth is too rapid to be observed in progress with the ultimate chain termination length believed to be dictated by pore steric effects to generate a bonded alkoxide in the long oligomer/short polymer length scale. At low temperatures, the rate-limiting step proceeds slowly so that considerable populations of unreacted propene are still observed up to 270 K. Full conversion of the propene is complete by 293 K resulting in a primarily linear mixture of products.

## EXPERIMENTAL METHODS

The ZSM-5 zeolite used was a powder form supplied by Johnson Matthey and calcined in air for 12 h at 773 K to remove the residual synthesis template. Characterization of the catalyst showed it to possess a Si:Al ratio of 30:1, established by SS-NMR, and a BET surface area of 370 m<sup>2</sup>/g.

Pretreatment of the zeolite to remove adsorbed water was carried out using a catalyst preparation gas-handling rig located at the ISIS facility: technical details of this apparatus have been previously published.<sup>31</sup> Fifteen-gram batches of the calcined zeolite were loaded into a cylindrical steel cell equipped with gas-handling fittings, mounted on the preparation rig, heated to 623 K under flowing helium (0.15 slpm, CK gas, >99.999%) at 10 K/min, and held for 3 h to remove adsorbed water from the zeolite. The dried catalyst was cooled to ambient temperature, and the reactor is isolated for moving to an argon-filled glovebox (MBraun UniLab MB-20-G, [H<sub>2</sub>O] < 1 ppm, [O<sub>2</sub>] < 1 ppm) where the catalyst was transferred to the experimental environments.

For QENS analysis, 2.5 g of the pretreated zeolite was loaded into an aluminum QENS sample cell with a 2 mm annular spacing and equipped with a single gas inlet port and indium wire gaskets. This cell design is equipped with top- and bottom-mounted copper blocks containing thermocouples and thermal resistance heaters to allow control of the cell temperature: cooling during neutron data collection is

provided by the closed-cycle refrigerator (CCR), which forms part of the spectrometer sample environment. The sample was mounted on a gas-handling center stick and cooled to 200 K using dry ice, and the gas lines to the cell were kept at 293 K to prevent premature condensation of the propene. A container of a known volume was charged with  $3.9 \times 10^{-2}$  mol of propene, equating to 7 molecules of propene/zeolite unit cell using a gas handling rig. This was connected to the sample cell, and the propene was allowed to condense into the interior from the top down. The cell was left at 200 K for 30 min to allow the propene to diffuse through the zeolite as a liquid. This procedure has been previously shown to allow the introduction of the propene to the zeolite while preventing any oligomerization reactions from occurring.<sup>14</sup>

Measurement of the QENS spectra was performed using OSIRIS, a near-backscattering indirect geometry neutron spectrometer at the ISIS Neutron and Muon Source, which is optimized for measurements in the quasi-elastic region. The (PG002) reflection from the graphite analyzer crystals was used in all cases, which defined the energy resolution of 25.4  $\mu$ eV and an accessible momentum transfer range of 0.18–1.8  $\text{\AA}^{-1}$ .<sup>32</sup> The propene-loaded sample was inserted into OSIRIS and cooled from the dosing temperature to base temperature (20 K). A series of 50  $\mu$ A·h QENS spectra were taken at 5 K intervals from the base temperature to 300 K. The measurement time at each temperature was approximately 20 min, allowing ample time for reactions to reach a stable state.

For INS analysis, two samples of the pretreated zeolite were loaded into aluminum gas-handling sample cells. This cell design has an in-beam geometry consisting of a 50  $\times$  50  $\times$  10 mm flat plate and is equipped with indium wire gaskets, gas ports, and thermocouple/heater pairs at the top and bottom of the cell. When inserted in the INS spectrometer sample environment, the pipe to the lower gas port is positioned on the side of the sample oriented away from the neutron detector bank to prevent interference with the recorded spectrum. Measurements were performed on the ISIS facility's indirect geometry spectrometer TOSCA. Compared to the direct geometry instrument used for the preliminary investigations previously reported,<sup>14</sup> TOSCA offers inferior resolution at high energy transfer values but superior resolution in the 200–1600  $\text{cm}^{-1}$  region where changes due to intermediate formation are most likely to occur.<sup>33</sup>

The first sample was used to prepare a sample of oligomerized propene loaded at room temperature for comparison with the results previously reported.<sup>14</sup> The sample was mounted on a gas-handling center stick, inserted in TOSCA, and cooled to base temperature (<25 K) for collection of a spectrum of the empty zeolite to allow subtraction of the zeolite contributions in later analysis. The sample was then removed and allowed to return to 293 K. A buffer volume was charged with  $2.51 \times 10^{-2}$  mol of propene, equating to a loading level of 12.27 propene molecules/zeolite unit cell calculated from the 11.80 g dry mass of the zeolite, and used to introduce the propene to the cell through the top-mounted pipe connection. Thirty minutes was allowed for the reaction to proceed to completion followed by insertion into the TOSCA spectrometer, cooling to base temperature, and collection of the spectrum of the fully oligomerized sample.

The second sample of 10.5 g of dry zeolite was used to investigate the unreacted propene and the reaction in progress. A background scan of the empty zeolite was collected in the same manner as that of sample 1 followed by dosing of the



propene as a liquid. Due to the greater mass of zeolite and larger cell involved in these measurements, the decision was made to perform the dosing at lower temperatures than used for the QENS measurement to prevent the possibility of some oligomerization occurring due to improperly cooled hot spots in the catalyst bed. The cell was removed, and the gas lines were warmed to 293 K to prevent propene condensation, while the zeolite sample was maintained at 77 K by immersion of the sample cell in liquid nitrogen up to the level of the top of the catalyst bed. Propene was introduced into the cell through the top port connection using the same method as before with a buffer volume charge in this instance of  $1.29 \times 10^{-2}$  mol of propene, equating to a loading level of 6.97 propene molecules/zeolite unit cell. The sample was left in this condition to ensure all the available propene condensed into the sample-containing portion of the cell to prevent blocking of the inlet port by frozen propene: after 30 min, the whole can was immersed in liquid nitrogen to cool to 77 K in order to prevent any possibility of the cell temperature rising above the target diffusion temperature during thermal equilibration with the TOSCA sample environment. The loaded sample was returned to the TOSCA spectrometer and heated to 140 K using the cell-mounted heaters to melt the propene and allow it to diffuse through the sample as a liquid; 60 min was allocated for this process, and after which, the sample was cooled back to the base temperature, and a spectrum of the loaded sample was recorded.

Following collection of the unreacted propene/ZSM-5 spectrum, additional spectra were collected with the same sample following heating to a series of temperatures from 200 to 270 K. For each point, the sample cell was heated to the target temperature inside the TOSCA sample environment using the cell's integrated heaters. The sample was held at this temperature for 30 min to ensure an equilibrium temperature across the full depth of the catalyst and to allow any reactions to occur; it was then returned to base temperature for spectrum collection. Spectra were recorded at 200, 215, 225, 240, 255, and 270 K with values chosen by reference to the results of the QENS investigation. Following completion of this test sequence, the sample cell was removed from TOSCA, allowed to stand at 293 K overnight, and then returned to collect an end-state spectrum of the fully oligomerized sample. Finally, a spectrum of  $4.076 \times 10^{-2}$  mol of pure propene was collected for comparison purposes.

All data analysis tasks, including conversion of neutron time-of-flight data to energy transfer values and data binning to generate the spectra presented, were performed using the Mantid software package.<sup>34</sup>

In order to examine higher-energy regions of the vibrational spectrum in greater detail, a further sample of the zeolite was analyzed by diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) using an Agilent Carey 680 FTIR spectrometer equipped with a Harrick praying mantis beam accessory and heated sample cell with gas-flow capability. Spectra were collected from 4000 to 700  $\text{cm}^{-1}$  using a liquid nitrogen-cooled MCT detector with a resolution of 4  $\text{cm}^{-1}$  and averaged over 64 scans/spectrum. The zeolite was heated to 423 K at 5 K/min while purging with helium (25 mL/min) and held for 30 min to remove adsorbed water. The sample was cooled back to 293 K under continued flow, and a spectrum of the unloaded zeolite was collected. A 3 mL/min flow of propene was then introduced to the helium flow and passed through the sample for 1 min. The sample was purged

for 5 min to remove residual gaseous propene from the headspace of the sample cell followed by collection of the oligomerized propene/ZSM-5 spectrum.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.9b03503>.

Figures S1 and S2: 3900–2700  $\text{cm}^{-1}$  diffuse reflectance infrared spectrum of ZSM-5 before and after adsorption of propene at 293 K and 0–1600  $\text{cm}^{-1}$  TOSCA INS spectra of propene after absorption into ZSM-5 (PDF)

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

### Funding

Johnson Matthey PLC and the EPSRC are thanked for postgraduate student support (A.P.H. and A.Z.) under the industrial CASE scheme no. EP/P510506/1.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Johnson Matthey PLC is thanked for supplying the ZSM-5 zeolite and for financial support through the provision of industrial CASE studentships in partnership with the EPSRC (A.P.H., no. EP/P510506/1; A.Z. no. EP/N509176/1). The

Science and Technologies Facilities Council is thanked for the provision of neutron beamtime (allocation nos. RB1720047<sup>35</sup> and RB1720048<sup>36</sup>). The resources and support provided by the UK Catalysis Hub via membership of the UK Catalysis Hub consortium and funded by EPSRC (grant nos. EP/K014706/1, EP/K014668/1, EP/K014854/1, EP/K014714/1, and EP/M013219/1) are gratefully acknowledged.

## ABBREVIATIONS

INS, inelastic neutron scattering; QENS, quasi-elastic neutron scattering

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