ACS Catalysis

Research Article

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Time-Resolved Studies of Ethylene and Propylene Reactions in Zeolite H-MFI by In-Situ Fast IR Heating and UV Raman Spectroscopy

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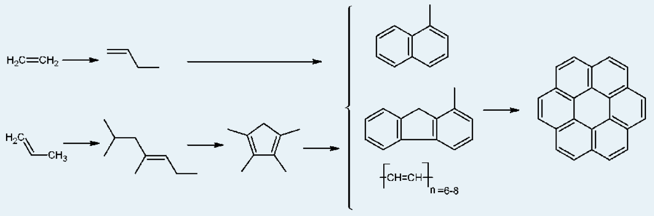
Ⓢ *Supporting Information*



ABSTRACT: The conversion of ethylene and propylene absorbed in zeolite H-MFI was studied using UV-Raman spectroscopy. To observe early stage reaction intermediates, an infrared laser was used as a fast heating source. Alkyl substituted naphthalenes and fluorenes, which have been previously suggested as hydrocarbon pool species, were observed regardless of the olefin reagent. Conjugated dienes were formed from propylene but not observed for ethylene at short reaction times. Conventional heating in a furnace was used to force the reaction to completion. For propylene sheet-like polyaromatic hydrocarbons were formed immediately. For ethylene cyclic dienes, conjugated olefins, and ultimately sheet-like polyaromatic hydrocarbons were formed at progressively higher reaction temperatures. The results show that the polyaromatic species implicated as deactivating coke in zeolite catalysts can be formed by conversion of polyenes.

KEYWORDS: *ethylene, propylene, UV-Raman, coke, zeolite, H-MFI*

■ INTRODUCTION

The conversion of methanol to hydrocarbons over zeolite H-MFI has been of great interest since it was used to synthesize gasoline beginning in the 1970s. Several reaction mechanisms have been proposed in the literature, but the most accepted idea today is one of a hydrocarbon pool mechanism, which was originally proposed by Dahl and Kolboe.[1−4] Much research has been done to identify the important species in the hydrocarbon pool and how they evolve during the life of the catalyst.

UV-Raman spectroscopy has been previously used for studying catalytic reactions.[5−7] UV-Raman spectroscopy can provide in situ vibrational information about the molecules formed during the reaction. As compared to infrared spectroscopy UV-Raman spectroscopy is particularly sensitive to hydrocarbon unsaturation represented by olefinic and aromatic structures. This technique has been used to study the methanol-to-hydrocarbons reaction over H-MFI.[8−10] However it is difficult to identify the early stage reaction products which are participating in the hydrocarbon pool, or even to identify the number of product molecules (or types of product molecules) formed. Without this information it is difficult to assign the Raman peaks as some may be from the same molecule. In particular, many of the bands overlap so it is not clear when in the reaction they begin to form and how they evolve with changes in reaction time and temperature. Two bands that appear at the same time and grow at a similar rate would likely be from the same molecule.

When methanol reacts at 77−127 °C over zeolites with relatively high Al content (Si/Al = 19−24) the primary products are propylene, ethylene, and some butene.[11,12] As the Si/Al ratio increases butene selectivity increases while ethylene formation decreases. Propylene remains a major product.[13] As the reaction temperature increases, ethylene is still formed but as a cracking product rather than a primary product.[14] Therefore, reaction studies starting with reactant molecules other than methanol, such as ethylene and propylene, may provide information about reactions in the zeolite that accompany methanol conversion.

According to molecular dynamics simulations ethylene molecules in concentrations of 8 molecules/unit cell preferentially sit in channel intersections, especially near Al substitutions.[15] The induced dipole moment of ethylene depends on its position in the porous structure. The molecules are most polarized in the channel intersections, causing them to be more reactive.[15] Semiempirical modeling shows an ethylene molecule reacts with a hydroxyl group in the zeolite forming a π-complex and the transfer of an electron to the zeolite framework.[16−18] This causes the formation of an ethylcarbenium ion which will react with other molecules (ethylene or other products) faster than it will desorb as gaseous ethylene. This molecular growth around the carbenium ion can result in polyethylene oligomers that will form other species at elevated temperatures.[12] The oligomers will be primarily dimers, though at high aluminum content (Si/Al ≤ 40) there will be larger oligomers as well.[19] The primary products of ethylene reacting on H-MFI (Si/Al = 19) at 300 °C are propylene, butanes,

Special Issue: Operando and In Situ Studies of Catalysis

Received: June 30, 2012
Revised: September 23, 2012
Published: October 3, 2012

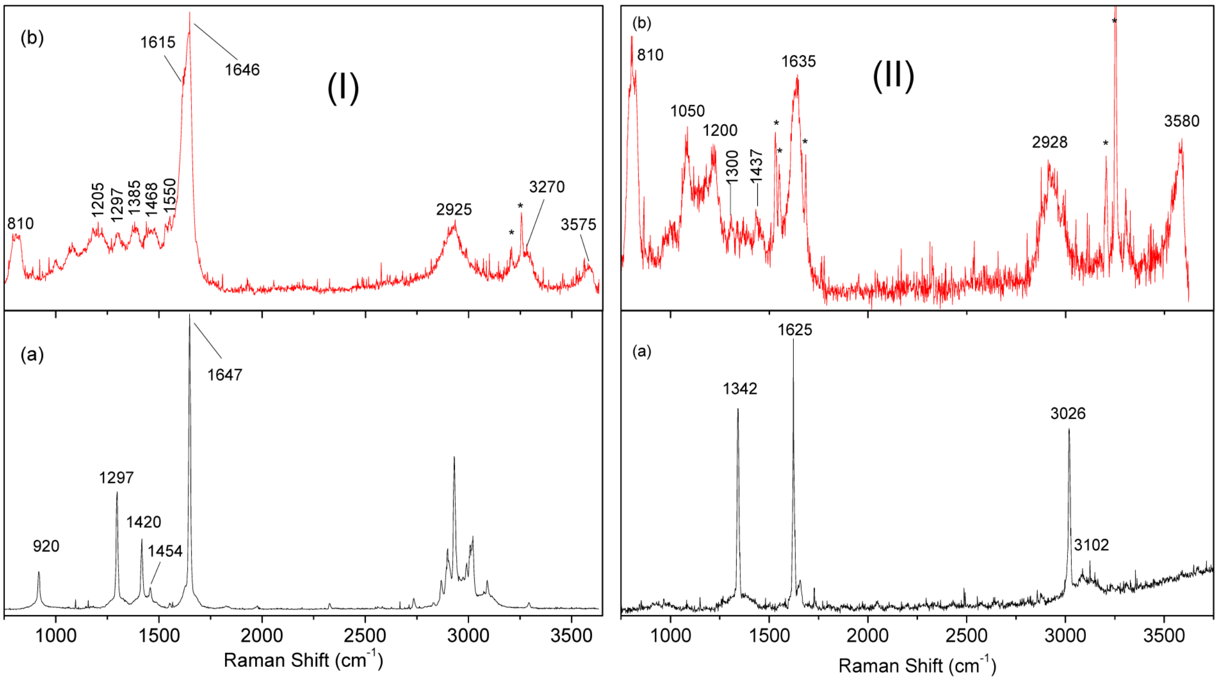


Figure 1. UV-Raman spectra of (I) (a) propylene gas and (b) propylene adsorbed in zeolite H-MFI, Si/Al = 18.5, (II) (a) ethylene gas and (b) ethylene adsorbed in zeolite H-MFI, Si/Al = 18.5 (* = plasma lines from laser).

isobutene, and isopentane.[20] Oligomerization is also reported for propylene.[21,22]

The Haw group suggests methylbenzenes and cyclopentenyl cations are particularly important components of the hydrocarbon pool formed from methanol and that their evolution to polyaromatic hydrocarbons is responsible for catalyst deactivation by coking.[23,24] They also report the formation of 1,3-dimethylcyclopentadienyl cation initially and subsequently toluene and other methyl-substituted benzenes from the reaction of ethylene in zeolite H-MFI at 350 °C, but the cyclopentadienyl cation is present at reaction temperatures as low as 100 °C.[25]

There is one fundamental difference between small alkenes dosed into a zeolite and alkenes formed from methanol in the zeolite: the presence of water. Reactants are generally dosed into a dry zeolite, but when ethylene and propylene form during methanol reactions water is released. The reaction of ethylene in the zeolite can change with the hydration level of the zeolite. Ethylene can oligomerize at room temperature in the zeolite, but not in the presence of methanol, dimethyl ether, or water. When these coreactants are present, no room temperature reaction occurs. Ethylene and water form ethanol at 160 °C and aliphatic hydrocarbons at 250 °C.[26,27]

In this work ethylene and propylene react over dry zeolite H-MFI. UV-Raman spectroscopy is used to identify the main products formed at various stages of reaction. To look closely at the early stages of reaction, an infrared (IR) laser is used as a fast heating source. After the sample is heated for a very short time (on the order of milliseconds) it is cooled and the products are observed by Raman spectroscopy. Using this pulse-quench method of heating, the products through various stages of reaction can be observed and identified. Subsequently, conventional heating using a furnace is performed so that the results produced by different heating methods can be compared. The results indicate that there is a route to the deactivation of the zeolite by polycyclic aromatic hydrocarbons that does not involve methyl benzenes as intermediates.

EXPERIMENTAL SECTION

Sample Preparation. Samples of zeolite H-MFI were kindly provided by Dr. Jeff Miller of Argonne National Lab (formerly of BP Chemical). The powders were first pressed into pellets, lightly ground, and sieved into particles ~100 μm in diameter. Approximately 100 mg of the pure zeolite (Si/Al = 18.5) was placed on a porous stainless steel disk in a home-built, stirred-bed reactor described in detail previously.[8] The sample was sealed from air by a quartz cover, with a gas inlet and outlet line to allow controlled exposure to gaseous reagents. The zeolite was calcined in oxygen (60 mL/min) at 600 °C for 2 h prior to reaction. The sample was then cooled to room temperature under helium flow (60 mL/min).

Ethylene (Matheson Tri-Gas, 99.95%, ultra high purity), propylene (Matheson Tri-Gas, 99.99%, research purity), and ethylene-d_4 (Sigma-Aldrich, 99% purity, 99 atom % D) were reacted in the zeolite. Gas phase reactants flowed over the zeolite at 10 mL/min for 30 s per dose (in 60 mL/min of helium). A 30 s dose is equal to 12 molecules per unit cell of each reagent for 100 mg of zeolite. The sample was flushed with helium for 5 min to remove weakly bound reactants and to allow equilibration within the zeolite. Dosing was repeated as desired throughout the reaction.

Raman Spectroscopy Experiments. UV Raman measurements were collected using the spectrometer described previously.[28] The 244 nm argon ion UV laser was aimed at the sample through a quartz window. The laser power was kept below 5 mW to prevent sample damage by the laser. Helium gas flow and mechanical vibration were used to stir the zeolite powder to further avoid laser damage. All spectra are an average of 4 scans collected for 400 s each.

A 9.3 μm infrared CO_2 laser with computer-controlled steering optics for controlling the laser power and position

(Synrad 48-2-93 and FH Index) were used to heat the sample. The laser was directed through a BaF_2 window on the side of the reactor and focused on the surface of the sample at an angle of 22.5°. By controlling the laser power and sweeping the beam in a pattern across the top of the powder it was possible to produce controllable temperature spikes in the range 50−600 °C with a duration of ∼1 ms. Peak temperatures during IR heating were calculated from the optical and thermal properties of the zeolite H-MFI, the IR laser power density, and the sweep rate of the beam across the powder surface. The calculated temperatures were in good agreement with the known temperature dependent conversion of methanol absorbed in the zeolite.[9] Further details of the IR laser heating procedure can be found elsewhere.[29] The sample temperature was determined by laser power and sweep rate. For these experiments, samples were heated to 100, 200, and 300 °C after olefin dosing. At each temperature, laser heating intervals starting at 60 s were gradually increased over 10 intervals to 600 s before continuing to the next temperature. A spectrum at room temperature in flowing helium was collected after each heat treatment. When two consecutive spectra showed no changes in peak positions, shapes, or intensities (see Supporting Information, Figure 1), the time, or temperature was increased.

After IR laser heating was completed, conventional heating was performed on the same sample. The propylene sample was heated at 3 °C/min to 150 °C and held for 5 min before spectral acquisition at elevated temperature. Consecutive spectra showed no changes indicating that any transformations had gone to completion. For ethylene, the heating process was extended to 250 and 350 °C. Samples were then cooled to room temperature and held under dry helium flow (10 mL/min) for 15 h. Raman spectra were collected the following day at room temperature. Throughout this procedure, the sample was never exposed to air. Raman spectra showed no indication of water in the sample.

Gas phase spectra of pure ethylene and propylene were obtained by removing the porous disk and performing the measurement on the undiluted gas flowing at 10 mL/min.

■ RESULTS

Adsorption in H-MFI (Si/Al = 18.5). UV-Raman spectra of gas phase propylene and ethylene are shown in Figure 1 panels Ia and IIa. The spectra compare well with the literature.[30,31] When the olefin gases are dosed into the zeolite at room temperature, there is immediate evidence of oligomerization. Oligomerization at room temperature has been previously observed in H-MFI.[22,27,32] Figure 1 shows a comparison between the gas phase spectra and spectra of the adsorbed molecule for both ethylene and propylene.

The first region that shows evidence of oligomerization is the CH stretching region. The pure propylene gas spectrum shows several sharp Raman bands from 2900 to 3100 cm^{-1}. However, for propylene loaded into the zeolite this region becomes one broad band at 2928 cm^{-1} with no distinguishable peaks. The width of the peak and the absence of sharp features are due to spectral overlap between oligomers with different chain lengths and in different environments within the zeolite. The absence of spectral features above 3000 cm^{-1} indicates that there are no detectable vinylic CH groups remaining in the oligomer. Similarly, ethylene shows peaks in the gas phase spectrum at 3026 and 3102 cm^{-1} due to symmetric and asymmetric CH_2 stretches, respectively. The spectrum of the absorbed ethylene exhibits a broad band at 2928 cm^{-1}, assigned to alkyl CH stretches,[33,34] and no intensity above 3000 cm^{-1}.

Other bands from the gas phase molecules are not detectable in the absorbed species. In propylene, ν(C−C) at 916 cm^{-1} and $\delta(CH_2)$ at 1420 cm^{-1} are not detected. In ethylene, the vinylic CH_2 scissor vibration at 1342 cm^{-1} is not present.

The presence of alkyl bands assigned to oligomers is evident. In the propylene case, a band at 1468 cm^{-1} has been assigned to the CH_3 asymmetric deformation of polypropylene oligomer, and can be used as an indicator of oligomer formation.[32,35] Other peaks at 1205 and 1385 cm^{-1} are also assigned to the polypropylene CH_2 twist/bend and the CH_3 symmetric deformation, respectively.[35] The band at 1297 cm^{-1} may be assigned to the CH bend of either polypropylene or residual, unreacted molecular propylene. In the spectrum of ethylene adsorbed in the zeolite, a small band at 1300 cm^{-1} is assigned to a CH_2 twist, and a band at 1437 cm^{-1} represents a CH_2 bending vibration of polyethylene formed inside the zeolite.

For ethylene, a peak assigned to the C═C stretch is seen in both the gas phase (at 1625 cm^{-1}) and the spectrum of the adsorbed molecule (at 1635 cm^{-1}). This peak signifies the presence of remaining C═C bonds in the oligomer. The substantial broadening of this peak for absorbed ethylene compared to the gas phase is due to the same factors that are responsible for the broadening of the bands in the alkyl CH stretch region. Likewise for propylene, a band at 1646 cm^{-1} due to C═C is present in the spectrum of the adsorbed molecule, but it is now overlapping with a peak at 1615 cm^{-1}. Both peaks have been observed previously by infrared spectroscopy.[32] The band at 1646 cm^{-1} is the expected band position for unreacted propylene monomers, as well as dimers (hexene) and trimers (nonene). A band at 1615 cm^{-1} signifies the presence of polyene or polycyclic aromatic hydrocarbons. Small amounts of coke have been reported to form at room temperature from propylene, consistent with the observation of this band.[36] A band at 3575 cm^{-1} is due to hydrogen-bonded OH groups in the zeolite structure. The band at 810 cm^{-1} is due to the zeolite framework vibrations.

A broad band at 3270 cm^{-1} in the spectrum of absorbed propylene is due to overtones of the fundamental vibrations in the region 1615 to 1646 cm^{-1}. The overtone from absorbed ethylene is less distinct because of overlapping laser plasma lines, but its intensity, relative to the peak in the 1600 cm^{-1} region, is approximately the same. Since the same dose was used for each olefin, the higher intensity in the 1600 cm^{-1} and overtone regions observed for propylene compared to ethylene signifies a greater degree of transformation. UV-Raman spectra of polyaromatic hydrocarbons (see Supporting Information, Figures 2−4) indicate that only conjugated dienes (Supporting Information, Figure 4) exhibit this overtone. Additionally, the fundamental vibrations of these conjugated dienes are near 1640 cm^{-1}, which is at higher Raman shift than the ring vibrations in fused ring aromatics (see, for example, Supporting Information, Figure 5) and very close to the 1646 cm^{-1} peak in absorbed propylene. These features signify that ethylene and propylene form conjugated dienes in the zeolite at room temperature.

Infrared Laser Heating. The spectra produced by progressive IR heating are seen in Figure 2 (ethylene) and Figure 3 (propylene). The same heating procedure was used for both reagents. Heating times range from 60 s to 10 min in a series of five treatments. The spectra reported here were

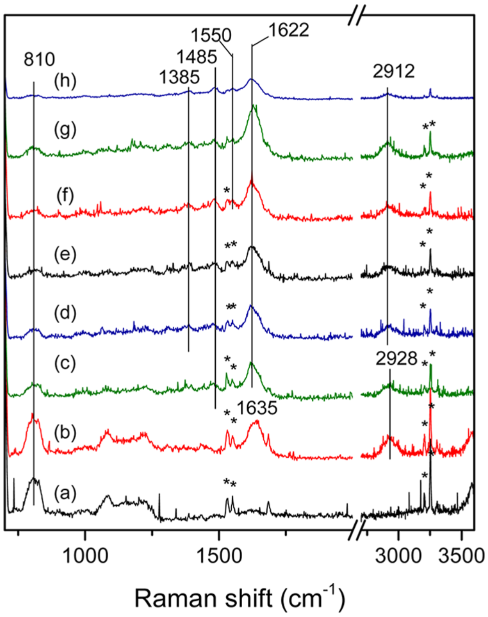


Figure 2. UV-Raman spectra of (a) Zeolite H-MFI, Si/Al = 18.5, (b) after 30 s ethylene dose, (c) after laser heating to 100 °C, (d) after 30 s ethylene dose (e) after laser heating to 200 °C, (f) after laser heating to 300 °C, (g) after sitting overnight at room temperature, (h) after laser heating to 300 °C .

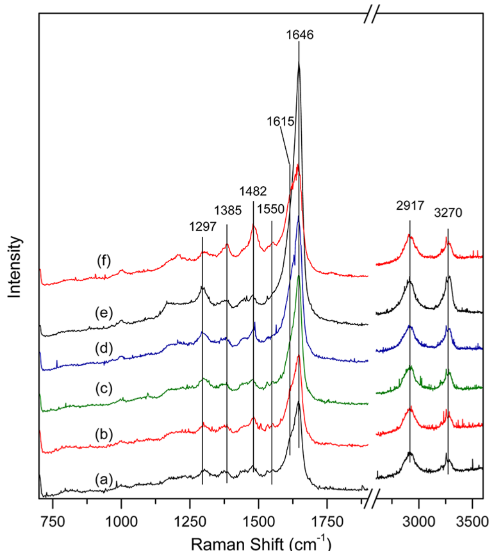


Figure 3. UV-Raman spectra of a 30 s propylene dose into Zeolite H-MFI, Si/Al = 18.5: (a) after laser heating to 100 °C, (b) after laser heating to 200 °C, (c) after 30 s propylene dose, (d) after laser heating to 300 °C, (e) after sitting overnight at room temperature (f) after laser heating to 300 °C.

collected after the 10 min heat treatment. Treatment temperatures increased from 100 °C (2c, 3a) to 200 °C (2e, 3b) to 300 °C (2f, 3d). Before spectra 2d and 3c a second 30 s dose of reactant was performed. Before spectra 2g and 3e the samples were held at room temperature under helium flow (10 mL/min) for 15 h. Subsequently, the samples were heated to 300 °C prior to measuring spectra 2h and 3f.

The results of the infrared heating are summarized in Table 1. There are several differences of interest between the ethylene and the propylene experiments. For ethylene, the zeolite peaks become weaker with time, consistent with self-absorption due

Table 1. Summary of the Results Shown in Figures 3 and 4

approximate peak position	800, 1050–1200 cm^{-1} (zeolite peaks)		1635 cm^{-1}		1480 cm^{-1}		1385 cm^{-1}	2912 cm^{-1}
	ethylene	propylene	ethylene	propylene	ethylene	propylene	ethylene	ethylene
100 °C spectra (c)	weakens slightly, indicating self-absorption	disappears after initial heating, indicating self-absorption	changes shape, shifts from 1635 cm^{-1} to 1622 cm^{-1}	1646 cm^{-1} peak increases relative to 1615 cm^{-1} peak	appears after 10 min of heating	appears after 10 min of heating	appears after 3 min of heating	after heating grows from half to equal intensity of 810 cm^{-1} peak
200 °C–300 °C spectra (d–f)				1646 cm^{-1} peak continues to increase	increases in intensity	increases in intensity	grows sharper	grows in intensity relative to 810 cm^{-1} peak
overnight (room temperature) spectra (g)	little change during subsequent heating		no change		unchanged	unchanged	unchanged	
300 °C (next day) spectra (h)				1646 cm^{-1} peak decreases relative to 1615 cm^{-1} peak	increases in intensity	increases in intensity	increases in intensity	reaches peak height of double the 810 cm^{-1} peak

to the formation of coke species. For propylene, the T-O-T zeolite band at 810 cm^{-1} is detectable after room temperature dosing but disappears completely after heating to just 100 °C. Because the amount of ethylene and propylene dosed was the same, this difference in behavior is due to the higher reactivity of propylene in the zeolite. Reaction products formed by propylene that absorb the 244 nm laser cause strong self-absorption resulting in the complete disappearance of the zeolite peak. Since saturated hydrocarbons, alkoxide, and benzene derivatives do not absorb strongly near 244 nm, the observation of self-absorption is another indicator for the formation of conjugated olefin and polycyclic aromatic species that absorb strongly in this region.

In the propylene experiment, there are changes in the relative intensity of the 1615 and 1646 cm^{-1} bands throughout the IR heating. In (3a)-(3e) the 1646 cm^{-1} band increases relative to 1615 cm^{-1} and all the other bands in the spectrum, particularly during the 15 h hold. It decreases in the final spectrum (3f) after IR heating to 300 °C. The peaks associated with the propylene oligomers (1205, 1297, 1385, and 1480 cm^{-1}) do not change in intensity during laser heating. After the room temperature hold they remain the same, but upon IR heating to 300 °C they increase in intensity, and a 1550 cm^{-1} peak appears in the spectrum. There is also a small band at 1000 cm^{-1} which indicates the presence of a single-ring-aromatic, such as benzene or a methyl-benzene, has formed,.

After completion of the IR heating series the spectra from reacted propylene and ethylene look very similar. The spectra in Figure 4 show that the two reagents exhibit nearly the same peaks and relative intensities. Three notable exceptions are a peak at 1297 cm^{-1}, a higher Raman shift for the peak in the envelope of the band in the 1610−1650 cm^{-1} region and the higher intensity of the overtone band near 3200 cm^{-1} in the propylene spectrum. The peak at 1297 cm^{-1} is assigned to the tertiary carbon CH bend, not expected for oligomers derived from ethylene. The latter two features signify that propylene produced a higher population of conjugated diene structures.

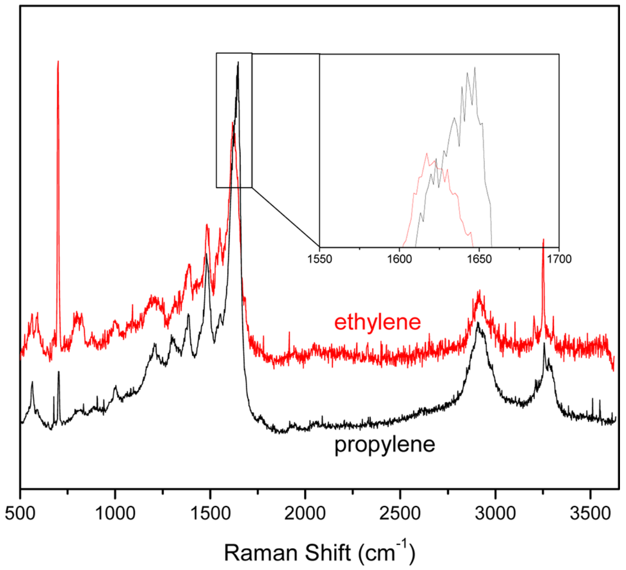


Figure 4. Comparison of UV-Raman spectrum of propylene (black) and ethylene (red) after 10 min of IR heating at 300 °C.

Conventional Heating. In the propylene experiment, conventional heating to 150 °C for 5 min leads to a loss of all peaks associated with polypropylene, as seen in Figure 5. The spectrum is dominated by one, broad, intense peak at 1615 cm^{-1} that can be assigned primarily to polycyclic aromatics. There are also two small peaks at 1186 and 1390 cm^{-1}. The disappearance of the broad band near 2900 cm^{-1} indicates the loss of CH groups, consistent with aromatization. The overtone band at 3270 cm^{-1} shifts to 3220 cm^{-1}, consistent with the shift of the two fundamental bands at 1615 and 1646 cm^{-1} to one band at 1615 cm^{-1}. The presence of this band indicates that residual conjugated dienes remain in the zeolite. The coking rate of propylene over H-MFI at 120 °C is very fast, so the complete conversion observed at 150 °C in this experiment is not unexpected.[36,37]

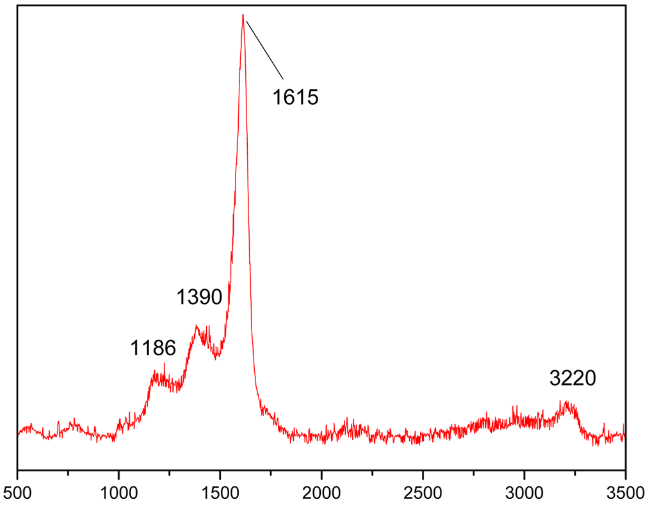


Figure 5. UV-Raman spectra of propylene in zeolite H-MFI after conventional oven heating to 150 °C.

Conventional heating of the species derived from ethylene presents a more interesting picture (Figure 6). After heating to 150 °C, the strongest band is at 1482 cm^{-1}. The 1622 cm^{-1} band has shifted to 1611 cm^{-1}, and the band at 1550 cm^{-1} has become more distinct. The 2903 cm^{-1} band has shifted slightly from its previous position at 2912 cm^{-1}, and the overtone has disappeared. The 810 cm^{-1} zeolite band has disappeared. The positions and relative intensities of the bands at 1000, 1207, and 1386 cm^{-1} remain essentially unchanged. Further heating to 250 °C leads to the band at 1550 cm^{-1} growing to approximately the same intensity as the 1485 cm^{-1} (shifted from 1482 cm^{-1}). The relative intensities of the bands at 1008, 1208, 1384, 1485, and 1611 cm^{-1} remain approximately constant. The 1208 and 1384 cm^{-1} peaks are sharper and more distinct. There is a slight increase in the intensity of the 2903 cm^{-1} band but no shift in position. After increasing the temperature to 350 °C, the strongest band in the spectrum is at 1550 cm^{-1}, followed by 1606 cm^{-1} (shifted from 1611 cm^{-1}). The band at 1485 cm^{-1} is no longer detectable. A trio of bands at 1417, 1395, and 1355 cm^{-1} (in order of decreasing intensity) replace the lone band at 1385 cm^{-1}. Careful inspection shows the bands at 1355 and 1417 cm^{-1} are actually present after lower temperature treatments, but they are not prominent until 350 °C. The sharp 1208 cm^{-1} band has been replaced by a prominent peak at 1156 cm^{-1}. The band at 1008 cm^{-1} is weaker but still detectable. The 2931 cm^{-1} band has decreased in intensity and has shifted significantly (from 2903 cm^{-1}). A broad feature centered at 3105 cm^{-1} is also visible. Finally,

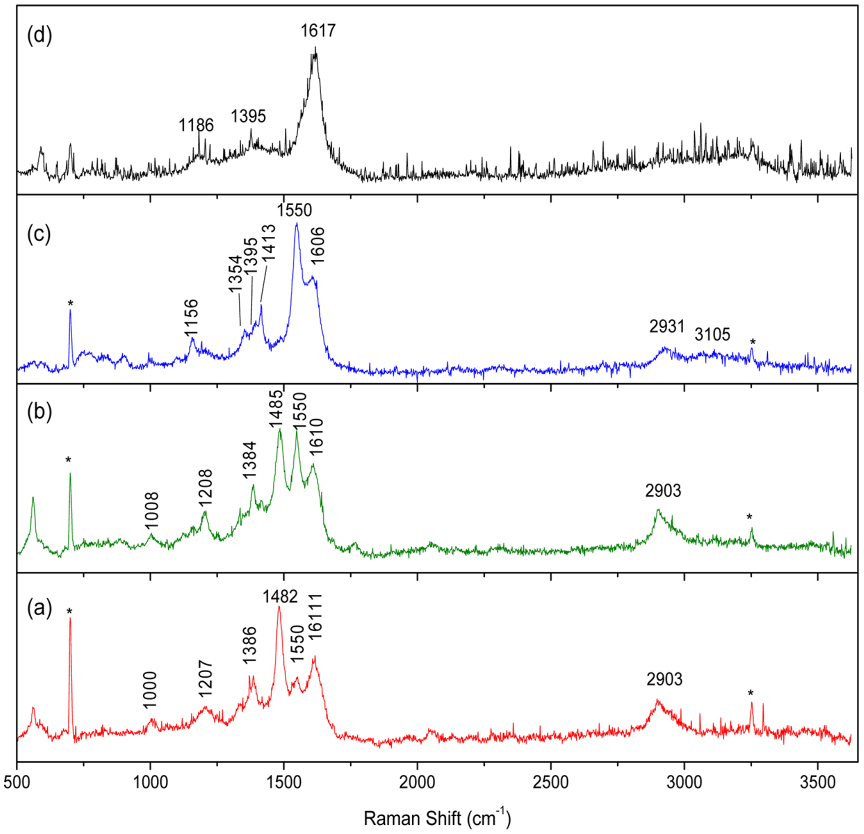


Figure 6. UV-Raman spectra of ethylene dosed after conventional heating to (a) 150 °C, (b) 250 °C, (c) 350 °C, and (d) after cooling to room temperature and holding for 15 h. (* - plasma lines from laser).

when the sample is left for 15 h at room temperature, Figure 6d, the bands at 1550 and 2931 cm^{-1} disappear from the spectrum. The main remaining peak is at 1617 cm^{-1} (shifted from 1606 cm^{-1}). There are small peaks at 1186 and 1395 cm^{-1}. This final spectrum looks much like the propylene experiment after heating to 150 °C.

■ DISCUSSION

There are three main stages in the experiment. In the first stage, IR laser heating, three main peaks were observed at 1385, 1480, and 1622 cm^{-1}. When the sample was held for 15 h the peaks remained in the same position, though the 1385 and 1480 cm^{-1} peaks decreased in intensity relative to the 1622 cm^{-1} peak. In the second stage, reheating with the IR laser after the 15-h hold, the peaks returned to their original intensities relative to each other. Finally, with the third stage, conventional heating, peaks at 1480, 1550, and 1615 cm^{-1} change relative intensity with varying temperature. Because the peaks around 1385, 1480, 1550, and 1615−1622 cm^{-1} all change intensity independently of one another, the data clearly supports at least four types of molecules being formed during the ethylene reaction.

IR Heating. There are two main differences between heating with the infrared laser and traditional heating with a conventional oven. The first is that the time scale of the heating and cooling is much shorter. A particle is hot for 10^{-3} to 10^{-6} seconds in laser heating, whereas in conventional heating the particle is hot on the order of minutes. The second is that only a small portion of the sample is heated at any instant of time by the IR laser, although the sample as a whole experiences the same heat treatment as the laser is swept across the top of the bed and the powder particles move as a consequence of stirring. The result of these two effects is that the range of thermally activated diffusion is very much smaller for IR heating than conventional heating. Near room temperature, ethylene diffuses at a rate of 1.5 $\mu m^2/ms$ through the zeolite.[15,38] Because the zeolite particles are sieved to be 100 μm in diameter, only gas phase products extremely close to the edges of the zeolite would have time to diffuse out before the sample cools. Those molecules will be swept away in the helium flow and will not be detected by Raman spectroscopy. Therefore, any observed products formed during IR heating must either be trapped inside the zeolite pores or attached to the exterior of the zeolite.

Some examples of molecules that could be formed inside the zeolite and would remain trapped are alkyl-benzenes, alkyl-naphthalenes, and fluorenes. Also, dienes such as the 1,3-cyclopentadienyl cation, suggested by Haw and co-workers, could fit inside the pores. UV-Raman spectra of these molecules and many other hydrocarbons were collected and compared with data from the reaction experiments to identify the products being formed.

A peak at 1385 cm^{-1} is in the region of C−H bending or aromatic ring breathing vibrations of naphthalenes. Because the growth of this band does not correspond to the growth of bands in other C−H regions, this band is assigned to naphthalene and substituted naphthalenes. Considering that the short heating time is unlikely to break C−C bonds in the original olefins, propylene would be likely to form dimethylnaphthalenes ($C_{12}H_{12}$) from four monomers, while ethylene would be likely to form naphthalene ($C_{10}H_8$) or dimethylnaphthalenes from four or five monomers respectively. Methyl-substituted naphthalenes, shown in Supporting Information,

Figure 5, all have a prominent peak in this region. Since this peak can shift by up to 10 cm^{-1} between solution spectra and spectra of the adsorbed molecules, it is not possible to assign this peak to a specific methyl-substitution unambiguously.[8] All of these molecules can fit inside the zeolite pores. Bulkier dimethylnaphthalenes (such as 1,8-dimethylnaphthalene) have peaks at lower Raman shift. They would be unlikely to fit in the pores, and they are not observed by Raman spectroscopy.

A review of the literature suggests few hydrocarbons exhibit Raman bands near 1485 cm^{-1}. Hydrocarbon C−H bending motions are never observed higher than 1460 cm^{-1}. Of the molecules studied only species containing unsaturated, 5-membered rings (thought to be important in the conversion of methanol to olefins) exhibit a band in this region.[9,25,39,40] In particular, compounds containing an sp^3 hybridized carbon, such as furan, indene, fluorene, or cyclopenta[d,e,f]-phenanthrene (Supporting Information, Figures 2−4) exhibit a strong peak between 1450 and 1500 cm^{-1}. In other molecules the peak is between 1425 and 1450 cm^{-1}. Further conclusions can be drawn about the identity of the molecule that gives rise to this peak based on the conventional heating portion of the experiment.

The peak at 1620 cm^{-1} is representative of polycyclic aromatic hydrocarbons. On the basis of the IR heating data, few conclusions can be drawn about the identity of these species, but they will be discussed further in connection with the conventional heating experiment.

Fifteen Hour Hold. When the products derived from IR heating of absorbed ethylene are left for 15 h at room temperature under helium flow, several changes are seen in the spectra. For both reagents the band intensities in the 1610−1646 cm^{-1} region increase relative to the other peaks. For propylene the peak intensity at 1646 cm^{-1} grows relative to that at 1615 cm^{-1}. The 1646 cm^{-1} peak decreases to a value below its intensity before the 15-h hold after IR heating to 300 °C. The peak at 1297 cm^{-1} mimics the behavior of the 1646 cm^{-1} peak. The band intensities at 1482 and 1550 cm^{-1} also increase after the final IR heating. Evidently the hydrocarbon species undergo aging at room temperature to precursors that form the species responsible for these bands upon further IR heating. The molecular nature of these species will be discussed in the next section.

Conventional Heating. Previously the band at 1550 cm^{-1} has been assigned to polyenes.[9] Polyenes produce a strong peak in this region, and there is a dependence on the number of C=C bonds and the Raman peak position. A peak at 1550 cm^{-1} corresponds to a polyene of the form $\left[\mathrm{C{=}C}\right]_n$ where $n = 7$.[41,42] Throughout the experiment from IR heating to 350 °C the peak remains sharp and does not shift. This means there is no evidence of either smaller or larger polyenes, only $n = 7$. Upon close inspection, the peak may be wide enough to include $n = 6$ and $n = 8$, but no additional polyene lengths. It is difficult to imagine how these polyenes could be formed at only this size and remain unchanged throughout further heating and reaction. Here we consider alternatives.

To investigate other possible assignments, UV-Raman spectra of many polyaromatic hydrocarbons were collected (see Supporting Information, Figures 2−4). While a few molecules such as 1,2,4,5-tetramethylbenzene, anthracene, benz[A]anthracene, benz[B]anthracene, and indene show a peak in this region, the 1550 cm^{-1} band is not the strongest in the spectrum meaning none of them can be responsible for the peak seen in Figure 6c. Methylation or ionization of an aromatic are possible explanations; however, there is no experimental evidence to support those assignments. Rather it appears likely that the initial assignment is correct and that the peak is from polyenes. This assignment is supported by the fact that the very strong 1550 cm^{-1} peak (from conventional heating) disappears completely after sitting for 15 h at room temperature. Polyenes are sufficiently reactive at room temperature to explain the observed transformation. In the propylene reaction, the fact that this peak is seen immediately after dosing indicates that the molecule is easy to form, and probably relatively small. Polyenes with a peak in this region would be formed by 6−8 propylene molecules. It has been shown in the literature that polyethylene and polypropylene oligomers containing 3−4 monomer units form at room temperature,[22,32] which suggests that polyenes of the required length can result by coupling and dehydrogenation of two oligomers. The fact that growth of the 1550 cm^{-1} band is most pronounced during conventional heating where diffusion in the zeolite is activated is consistent with the coupling mechanism.

The band at 1620 cm^{-1} has long been used to identify polycyclic aromatic hydrocarbons. Because this peak is present in all of the measured aromatics, it is difficult to make an assignment to a specific compound. In fact, the width of the peak suggests there are contributions from several types of molecules. In this data, shifts in the position may give clues to the identity of the molecules responsible for this band.

After dosing ethylene into the zeolite, a C=C stretch is present at 1635 cm^{-1}. After IR heating, the peak has shifted to 1622 cm^{-1}. This shift is large enough to indicate that the band is due to aromatic products, not to oligomerized ethylene in the zeolite. In fact several polycyclic aromatics which we would expect to see early in the reaction have peaks in this region, such as naphthalene (1633 cm^{-1}), alkylated naphthalene (1613−1638 cm^{-1}), and anthracene (1633 cm^{-1}). Since peaks from absorbed hydrocarbons can shift by 10 cm^{-1} compared to solid or solution phase spectra, the precise position of this peak cannot be used to make a specific assignment.[8]

As the reaction progresses via conventional heating, the peak shifts from 1622 cm^{-1} to 1611 cm^{-1} to 1606 cm^{-1}. The peak position in a number of fused-ring aromatic compounds is summarized in Table 2. Small, straight-chain molecules such as naphthalene, anthracene, and benz[B]anthracene show peaks at higher Raman shift (1633−1636 cm^{-1}), indicating they may be formed early in the reaction. Bent polycyclic chains such as in chrysene, benz[A]anthracene, dibenz[A,H]anthracene, and phenanthrene show peaks at lower Raman shift, 1604−1609 cm^{-1}. This suggests that over time and with increasing

Table 2. Band Positions of Fused Aromatic Molecules[40]

	molecule	band position (cm^{-1})
chains	naphthalene	1633
	anthracene	1633
	benz[B]anthracene	1636
bent chains	benz[A]anthracene	1609
	chrysene	1604
	dibenz[A,H]anthracene	1609
	phenanthrene	1605
sheets	triphenylene	1623
	pyrene	1633
	coronene	1628

temperature, the aromatic chains grow in length and form bent structures, possibly influenced by the structure of the zeolite pores. Sheet-like structures such as pyrene, triphenylene, and coronene are too large to fit inside the zeolite pores. Their higher Raman shifts (1623−1633 cm^{-1}) and the shift in the peak position during reaction to 1617 cm^{-1}, suggest that they may be formed on the outside of the zeolite with time and temperature.[40]

Finally, after the sample has been allowed to sit at room temperature for 15 h, the band center shifts back to 1617 cm^{-1}, and it is the only strong peak in the spectrum. This indicates a combination of bent chains (1604−1609 cm^{-1}) and sheet-like molecules (1623−1633 cm^{-1}) have formed, and alkyl CH groups are no longer present. Because of the size of the sheet-like molecules, they must be on the outside of the zeolite, while the bent chains may still be inside the pores.

In the propylene experiment, there are two overlapping peaks in this region, even at room temperature. Initially they are at 1615 and 1646 cm^{-1}. This makes it difficult to determine anything definite about products that show peaks in this area. However, some things can be noted. First, the ratio of the 1615 cm^{-1} and 1646 cm^{-1} bands changes throughout the reaction. All of the aromatics proposed to contribute to the 1600 cm^{-1} region have peaks at or below 1630 cm^{-1}, indicating that any products formed would overlap with the 1615 cm^{-1} side of the peak (see Table 2). If the entire region of the spectrum is fit to two peaks, the position of the 1646 cm^{-1} remains approximately constant throughout the reaction, while the other peak shifts from 1615 cm^{-1} to 1612 cm^{-1}. While this shift is small, it fits the trend seen in ethylene that as the reaction progresses, molecules get larger, chains bend, and this band moves to lower Raman shift.

The peak at 1389 cm^{-1}, assigned to naphthalene, shifts first to lower Raman shift (1384 cm^{-1}) and then up to 1395 cm^{-1}. The move to lower Raman shift is consistent with the addition of up to two methyl groups to the naphthalene molecule. Larger, similar molecules, such as anthracene or 2,3-benzanthracene have peaks at 1399 cm^{-1} and 1387 cm^{-1} respectively. This indicates that with prolonged heating, the naphthalene molecule may expand to include one or two additional rings.

To provide additional information about the assignment of the band near 1485 cm^{-1} spectra of furan, fluorene, and fluoranthene were compared with their totally deuterated analogues.[40] The ethylene experiment was then repeated using C_2D_4 (Supporting Information, Figure 6). From the magnitude of the shifts in the peaks with the deuterated reagent, some conclusions could be drawn about the nature of the cyclopentadienyl species. First, the shift upon deuteration is too small to be assigned as a CH (CD) bending vibration. In the reaction data deuteration causes the peak to appear at 1437 cm^{-1}, a down shift of 44 cm^{-1}. In furan, which is an isolated ring, the band shifts 70 cm^{-1}, much more than the reaction data. In fluorene the shift is 56 cm^{-1}. In the larger molecule fluoranthene the shift is similar to the reaction data, 46 cm^{-1}. However its fused ring structure does not have the sp^3 hybridized carbon in the ring that correlates with a high intensity band as alluded to previously. Instead, the most likely structure is a fluorene type molecule where the sp^3 carbon is not hydrogenated but alkylated. Because the 1480 cm^{-1} vibration involves the five-membered ring, changing the substitution on the sp^3 hybridized carbon from CH_3 to CD_3 would cause less of a shift than changing H to D on the ring.

Overall, the propylene experiment shows very similar results to the ethylene experiment, which is expected as these small olefins are assumed to contribute similarly to the formation of retained hydrocarbons in the pool mechanism.[1−4,43,44] In fact, after IR heating to 300 °C the spectra look very similar, as shown in Figure 4. Besides a peak at 1297 cm^{-1} which is assigned to polypropylene and is not present in polyethylene, there are 3 other major differences between the two spectra: (1) with propylene the 810 cm^{-1} zeolite peak is not detectable, (2) the position of the 1600 cm^{-1} region peak in ethylene is 1622 cm^{-1} whereas in propylene there are two overlapping peaks at 1612 cm^{-1} and 1645 cm^{-1}, and (3) in propylene there is a strong overtone band at 3270 cm^{-1} that is much weaker with ethylene. However, an important difference between the two reactants is their response to conventional heating at 150 °C. In the ethylene case, this produces more of the laser heating products (fluorenes and naphthalenes) to be formed which can be identified by strong sharp peaks in the spectra. In propylene, the reaction to form polycyclic aromatic hydrocarbons goes to completion at this temperature.

The model compounds that showed a large overtone in the 3200 cm^{-1} region were all dienes such as 1,2,3,4-tetramethyl-1,3-cyclopentaidene, tetramethyl(*n*-propyl)cyclopentadiene, 1,2,3,4,5-pentamethylcyclopentadiene, and 1,3-cyclohexadiene. Strong absorption by these dienes in the UV region produces resonance enhancement of the Raman intensity and is responsible for the strong overtone intensity at 3270 cm^{-1}. The strong absorption also causes self-absorption, resulting in the disappearance of the 810 cm^{-1} zeolite peak. Similarly, the consistently higher Raman shift for the peak in the 1600 cm^{-1} region derived from propylene reaction is in accord with the band position for dienes relative to fused ring aromatics.[40] The conventional heating data indicates that when the entire sample is heated, these dienes are very reactive with the aromatics (fluorenes and naphthalenes) that have been formed during IR laser heating. Both the small aromatics and the dienes are not present in the spectrum after 150 °C conventional heating when propylene is the reactant. When the concentration of these dienes is lower, as with ethylene, the fluorenes and naphthalenes continue to form during 150 °C, conventional heating.

■ CONCLUSIONS

Overall this research strongly supports the formation of retained hydrocarbons that are components of a pool such as suggested by Kolboe and Haw.[25,44,45] With increasing temperature and time, polymerized olefins give way to polyenes, straight- and bent-chain, alkyl-substituted polycyclic aromatic hydrocarbons (PAH), and finally sheet-like PAH. Previous work, particularly that of Haw and co-workers,[4,46] has shown that cyclopentadienyl species and methyl-benzenes are the primary catalytic hydrocarbon pool species and that the reaction pathway to polycyclic aromatics is through the alkylated, single-ring aromatics. These types of molecules are detectable by Raman, but were not observed to be major species in these experiments. Our work indicates that an important path is one that leads directly from polyolefins to polyenes to fused-ring aromatics analogous to the proposal by Shultz.[47−49] The major stable hydrocarbon species in our work are substituted naphthalenes and fluorenes. While propylene is more reactive than ethylene and there are differences in the specific compounds formed by each reactant (propylene favors the formation of more reactive dienes while ethylene does not) the reaction pathways appear to be generally the same, and the same final products are formed.

ASSOCIATED CONTENT

Supporting Information

Further details are given in supporting figures 1–6. This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding

Financial support of this work was provided by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy under Grant DE-FG02-97ER14789.

Notes

The authors declare no competing financial interest.

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