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LDRD Project Title: A New Approach to Fundamental Mechanism Discovery in Polymer Upcycling

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ABSTRACT:

We present a new experimental methodology for detailed experimental investigations of depolymerization reactions over solid catalysts. This project aims to address a critical need in fundamental research on chemical upcycling of polymers – the lack of rapid, sensitive, isomer-selective probing techniques for the detection of reaction intermediates and products. Our method combines a heterogeneous catalysis reactor for the study of multiphase (gas/polymer melt/solid) systems, coupled to a vacuum UV photoionization time-of-flight mass spectrometer. This apparatus draws on our expertise in probing complex gas-phase chemistry and enables high-throughput, detailed chemical speciation measurements of the gas phase above the catalyst, providing valuable information on the heterogeneous catalytic reactions.

Using this approach, we investigated the depolymerization of high-density polyethylene (HDPE) over Ir-doped zeolite catalysts. We showed that the product distribution was dominated by low-molecular weight alkenes with terminal C=C double bonds and revealed the presence of many methyl-substituted alkenes and alkanes, suggesting extensive methyl radical chemistry. In addition, we investigated the fundamental reactivity of model oligomer molecules *n*-butane and isobutane over ZSM-5 zeolites. We demonstrated the first direct detection of methyl radical intermediates, confirming the key role of methyl in zeolite-catalyzed activation of alkanes.

Our results show the potential of this experimental method to achieve deep insight into the complex depolymerization reactions and pave the way for detailed mechanistic studies, leading to increased fundamental understanding of key processes in chemical upcycling of polymers.

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INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS:

In 2019 the U.S. DOE Basic Energy Sciences Roundtable produced a report entitled *Chemical Upcycling of Polymers*,[1] concluding that "discarded plastics pose a long-term environmental challenge," and that "chemical upcycling of polymers…holds the promise of changing the paradigm for discarded plastic from waste to valued resource." The report identified the fundamental challenges that block an accelerated transformation of discarded plastics to higher-value materials. We aimed the work described in this SAND report directly at this challenge, with the goal of demonstrating a new approach to fundamental mechanism discovery in polymer deconstruction that is needed for the rational co-design of recyclable polymers and catalysts.

Existing literature shows that polymers can be thermally deconstructed into gas-phase and liquid-phase molecules, and that the required temperatures are lower in the presence of an appropriate catalyst.[2] Much of this research is optimization focused: finding the best pressures, temperatures, catalysts, and residence times to increase the yield of desired products. Although it is common in these publications to see mechanistic diagrams of chemical bond breaking and formation during the deconstruction process, almost all proposed mechanisms are based on how the coarse chemical characterization of final products (e.g., grouped quantification of alkanes, alkenes, aromatics) depends on processing parameters. In our assessment, the diagnostic tools currently applied to this problem significantly limit fundamental understanding. We proposed that rapid, isomer-selective detection of products and reactive intermediates in the gas phase would be an insightful new approach to elucidate mechanisms of catalytic depolymerization.

The workhorse tools in the literature for product evaluation in polymer deconstruction are Gas Chromatography coupled with Mass Spectrometry (GC/MS) for vaporized liquids and Thermal Conductivity Detection (GC/TCD) for gases.[3-8] Fourier Transform Infrared Spectroscopy (FTIR) is also used to provide functional group analysis of intact polymers, partially degraded polymers, and final products.[9, 10] Although GC/MS and GC/TCD can provide product identification, achieving true isomer-level selectivity requires complex and time-consuming measurements due to the need for multiple chromatography columns and to slow separation of different chemical species on each column. GC-based techniques also cannot detect closed-shell or open-shell reactive intermediates, which decay before or during analysis, taking with them the mechanistic clues encoded in the identity of such intermediates. FTIR spectroscopy can provide much faster response times, but without a species-sorting step – such as slow chromatography – the contributions of a mixture of species are overlaid onto a single infrared spectrum. That fact renders FTIR spectra useful for analysis at the functional group level (delineating alkenes vs. aromatics vs. ketones), but ineffective at identifying and quantifying specific molecules in the complex mixtures of products seen in depolymerization chemistry. FTIR also suffers from low sensitivity, and in most applications the inability to detect reactive intermediates. Researchers need a rapid, sensitive, and isomer-selective method that can observe not only products, but also reactive intermediates, including free radicals, where the unpaired electron makes radicals highly reactive and hence challenging to detect.

In this work we used Exploratory Express LDRD funds to create a new heterogeneous gas/solid catalysys test reactor (CTR). We coupled this reactor to existing photoionization mass spectrometry (PIMS) setups that use vacuum ultraviolet radiation to ionize molecules without excessive fragmentation. A complete description of the CTR/ PIMS instrument is given below, but at this point a summary is useful to underscore the promise of this technique for fundamental studies of depolymerization. As neutral gas-phase molecules desorb from solid catalysts or from the polymer/catalyst melt, they are rapidly extracted into a vacuum chamber with sufficiently low pressure that all collisions cease, and hence all chemistry stops, preserving any free radicals or other intermediates and products that may have desorbed from the decomposing polymer. After ionizing these neutral species, the resulting cations (all with +1 charge) are separated by mass (2 – 700 amu) in a mass spectrometer with an ultimate time resolution of 40 μs. By tuning the photon energy of the ionizing radiation, we acquire photoionization (PI) spectra of all masses simultaneously to identify and quantify the isomeric constituents at each mass. Together, these observables provide isomer-resolved species separation that is significantly faster than possible with GC, while also identifying hundreds of individual molecules simultaneously compared to the functional-group lumping that usually limits FTIR detection.

As a proof-of-principle demonstration, we investigated the depolymerization of the ubiquitous plastic high-density polyethylene (HDPE). HDPE is a high molecular weight polymer composed mainly of unbranched, saturated hydrocarbon chains. Literature mechanisms of both high-density and low-density polyethylene depolymerization generally center on the breaking of a C-C bond, forming two free radicals at the chain break, thereby cracking the very long polymer chains into shorter oligomers.[2] This “radical chain mechanism” can produce shorter saturated alkanes by recombination of two free radical chains, or formation of even shorter alkane + unsaturated alkene molecules by H transfer from one radical to the other (the disproportionation mechanism). In addition, methyl radicals (CH_3) have been proposed[6] as reactive intermediates that add to a radical site either at the terminal or internal C atom of another chain, generating branched hydrocarbons in the latter case. However, to the best of our knowledge, CH_3 radicals have not been detected to corroborate this mechanistic proposal. Finally, a reducing environment is often created by addition of molecular hydrogen (H_2) in an attempt to limit oxidation and promote the formation of fully saturated products.[7, 11]

We tested our approach on two types of experiments, both of which were done in a reducing environment of H_2. In test case #1 we flowed gaseous unbranched and branched oligomer surrogates n-butane and isobutane over solid ZSM-5 zeolite catalyst to probe the fundamental C-C and C-H bond scission trends of simple model compounds. In case #2 we investigated the deconstruction of HDPE over an iridium-doped zeolite (Ir-ZSM-5) catalyst to test whether our isomer-selective speciation measurement could illuminate the fundamental reactivity trends discovered in case #1, but in the context of a complex "real-world" depolymerization process. The group of Prof. Chao Wang of Johns Hopkins University provided the HDPE/Ir-ZSM-5 sample.

Our experiments provided several key results that demonstrate the promise of this approach:

- Test case #1 provides unambiguous detection of CH_3 radicals in the gas phase.
- Branched hydrocarbons are produced from unbranched n-butane reactant.
- Unbranched hydrocarbons are produced from branched isobutane reactant.
- Test case #2 showed that HDPE products are dominated by alkenes despite the reducing atmosphere.
- In addition to unbranched alkenes and alkanes, branched alkenes and alkanes are produced and quantified for $C_2 – C_6$ hydrocarbons, supporting methylation chemistry.
- The substitution of D_2 for H_2 in the feed gas induces full deuteration of some products, but partial, site-selective deuteration of others, demonstrating avenues for additional mechanistic insights.
- Specific aromatic compounds are produced at higher temperatures.

Although these results are preliminary, these first data demonstrate that gas-phase probing can offer valuable information on multi-phase processes, providing new understanding of fundamental mechanisms in the chemical upcycling of polymers.

DETAILED DESCRIPTION OF RESEARCH AND DEVELOPMENT AND METHODOLOGY:

Our goal is a proof-of-principle demonstration of a new method for rapid isomer-selective probing of chemical intermediates and products in catalytic depolymerization reactions. To achieve this, we designed a heterogeneous catalysis test reactor (CTR) and coupled it with multiplexed photoionization mass spectrometry (PIMS) detection, as shown schematically in **Figure 1**. The CTR is based on a high-pressure reactor, developed under DOE/BES funding for studies of gas-phase chemical kinetics, which was adapted to hold solid polymer and catalyst samples under a continuous gas flow at constant T and P. The original reactor was described in detail previously;[12] briefly, it has a 40 mm-long, 8 mm diameter bore inside of a heated Inconel chamber, capable of operating at T = 25 – 600°C and P = 0.01 – 100 bar. Precision mass flow controllers deliver up to five separate gas flows through an in-line helical gas mixer to the CTR, providing on-the-fly control of the chemical composition of the gas. After the reactor, gas exits to a pump; a feedback-driven needle valve maintains constant pressure in the CTR by throttling the pumping speed in the exhaust lines. This configuration enables independent control over the gas pressure and residence time in the CTR. The central portion of the gas flow is sampled from the CTR through an interchangeable pinhole nozzle (0.005 – 0.05 mm in diameter) into a vacuum chamber, creating a supersonic free-jet expansion. In the expansion the density and temperature of the gas drop rapidly such that molecular collisions and chemical reactions cease within several nozzle diameters, preserving the chemical composition of the gas, including unstable, highly reactive radicals and closed-shell molecules.

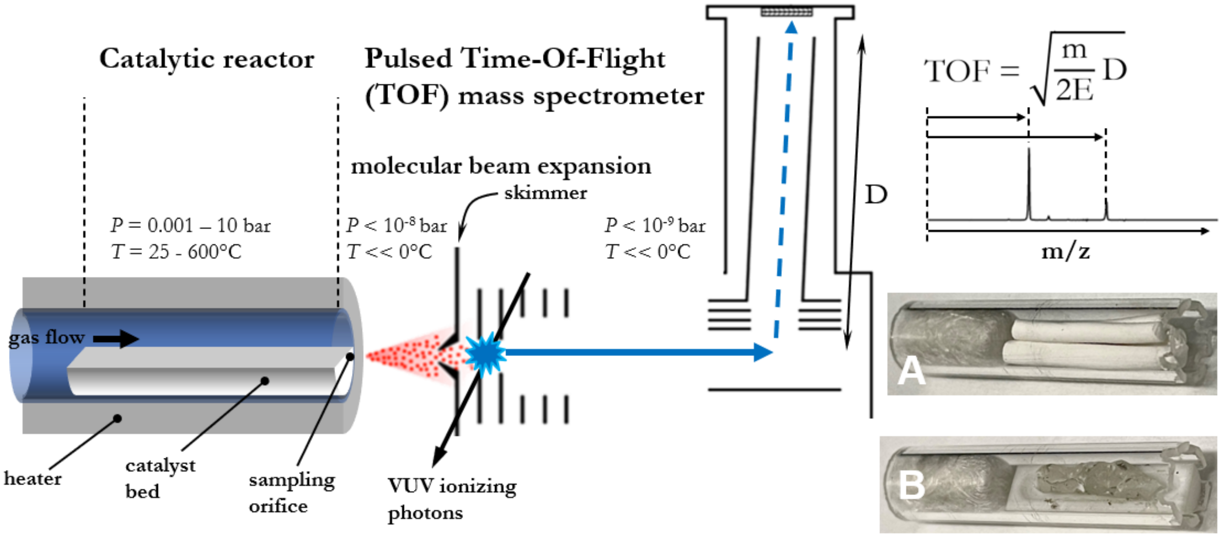

Figure 1. Schematic illustration of the experimental setup, which combines a high-pressure catalysys reactor with molecular beam gas sampling and a pulsed Time-Of-Flight (TOF) mass spectrometer. The insets A and B show the quartz reactor insert with glass wool at the entrance and either unmodified ZSM-5 zeolite rods (A) or a sample of HDPE, embedded with Ir-modified ZSM-5 zeolite powder (B).

In the present work the bore of the CTR was lined with an insert (inner diameter 6 mm) made of fused silica (insets A/B in **Figure 1**), which is chemically inert towards hydrocarbons even at elevated temperatures. Unmodified ZSM-5 catalyst rods or HDPE embedded with Ir-modified ZSM-5 (Ir-ZSM-5) powder were placed at the front of the CTR and held fast by a plug of gaspermeable fused silica wool at the upstream end. In some experiments, gaseous hydrocarbons (0.4 – 1% mole fraction) entrained in carrier gas flow (5 – 30% H_2 / balance He) were passed over the solid ZSM-5 rods, which were physically unchanged and retained shape throughout the experiments. Typical average residence times for the gas flow were 0.04 – 0.3s. Volatilized conversion products entered the carrier gas and were sampled out of the CTR for chemical analysis. In other studies, carrier gas (5 – 30% H_2 / balance He) flowed over the HDPE/Ir-ZSM-5 samples; depolymerization products that desorbed into the gas phase were entrained in the carrier gas flow and similarly sampled out of the CTR for analysis. Because HDPE melts when heated above ~200°C, the samples were placed in a 1.5 mm deep Macor (fluorphlogopite mica in borosilicate glass) holder at the bottom of the reactor to contain the melt.

The gas sampled from the CTR was analyzed by one of two MPIMS apparatus, developed under DOE/BES funding for studies of gas-phase chemistry.[12, 13] The principle of operation of both mass spectrometers is similar. Briefly, a beam of vacuum ultraviolet (VUV) light intersects the free-jet expansion and ionizes all molecules with ionization energy below the photon energy. The cations are focused into an ion beam, accelerated by a pulsed transverse electric field, and detected as a function of their time-of-flight (TOF), from which their mass-to-charge (*m/z*) ratio is determined. All ions are detected at once without switching mass channels, resulting in high-throughput, rapid measurements.

One of the MPIMS apparatus[13] in this project was used as an end-station at the Chemical Dynamics Beamline (9.0.2) of the Advanced Light Source (ALS), a 3rd-generation synchrotron facility at the Lawrence Berkeley National Laboratory. It used quasi-continuous, bright, narrowband tunable VUV radiation in the 8 – 12 eV range from a monochromator terminal at Beamline 9.0.2 for ionizing the sampled gas. Scanning the photon energy while collecting mass spectra at fixed reactor conditions provides photoionization (PI) spectra of each ion peak. From these spectra, chemical species with known PI cross-sections (PIXS) can be identified and quantified relative to a reference compound with known concentration and PIXS, as described previously.[14, 15] We found that at favorable conditions with strong ion signals 10 – 30 seconds of averaging at each photon energy produced high-quality PI spectra in just a few minutes of total acquisition time. Additionally, collecting mass spectra at fixed energies enables rapid surveys of the response of mass spectra to experimental conditions, albeit without separating chemical isomers at the same molecular mass. For example, the change in mass spectra due to varying P, T, residence time, or carrier gas composition can be measured with time resolution limited only by the required averaging time for high signal-to-noise ratios (typically less than a minute).

Because beamtime at the ALS is limited, we also performed experiments using a second MPIMS apparatus[12] in the laboratory at SNL, employing continuous VUV radiation from an H_2

discharge lamp. This photon source produces a broadband VUV spectrum, peaked at the Hydrogen Lyman-α line near 121.5 nm (10.2 eV); in the present work we used MgF_2 or LiF filters to limit the energy of the ionizing photons to below ~10.2 or ~11.5 eV, respectively. Although detailed chemical speciation is not possible with this VUV source, we used it to develop experimental protocols and to qualitatively gauge the distribution of molecular sizes and structural groups (e.g. alkenes vs. alkanes) as a function of CTR conditions.

RESULTS AND DISCUSSION:

Fundamental catalytic reactivity studies of model alkanes

Our first major objective was to probe the molecular structure dependent pathways in zeolite-catalyzed conversion of two model alkane compounds, *n*-butane and isobutane. The gas-phase C-H bond dissociation energies (BDEs) of the primary and secondary C atoms in *n*-butane are $\Delta_rH(0K) = 417.2$ kJ/mol and 405.3 kJ/mol, respectively. The primary and tertiary C atom C-H BDEs in isobutane are 419.2 kJ/mol and 397.7 kJ/mol, respectively. The terminal C_1-C_2 and internal C_2-C_3 BDEs are 336.6 kJ/mol and 360.6 kJ/mol in *n*-butane, respectively; the C-C BDE of isobutane is 361.2 kJ/mol.[16] These differences in gas-phase bond strengths may affect surface-catalyzed reactions, contributing to selectivity of dehydrogenation or C-C bond activation reactions. Furthermore, the structure specific catalyst interactions and reactions of specific bond scission products should differ from *n*-butane to isobutane, making them good starting points for fundamental studies of structure-dependent catalytic reactions.

Several experiments were conducted at Sandia by flowing gaseous *n*-butane and isobutane (5 – 30% H_2/0.4 – 1% C_4H_{10}/balance He) over unmodified ZSM-5 at total P ~ 800 Torr and T = 25 – 350°C. A typical mass spectrum, collected using the H_2 discharge lamp with a MgF_2 filter, is shown in **Figure 2** for *n*-butane at 350°C. The large ion peaks at $m/z = 58$, 42, and 43 correspond to the parent ion and dissociative ionization (DI) fragments of *n*-butane. The $m/z = 59$ ion peak is due to ^{13}C-substituted *n*-butane, which is naturally present at ~4.4%, relative to all–^{12}C *n*-butane. The $m/z = 56$ peak corresponds to the largest conversion product channel (C_4H_8), which we assign to unspecified butene isomers (1-butene, 2-butene, or isobutene). We also observed a minor product channel with a sum formula of pentene: C_5H_{10} ($m/z = 70$), along with four minor channels, consistent with aromatic products: C_6H_6 ($m/z = 78$), C_7H_8 ($m/z = 92$), C_8H_{10} ($m/z = 106$), and C_9H_{12} ($m/z = 120$). The same ion peaks (but with different intensities) were detected in the case of isobutane in the gas feed. These minor products result from zeolite-catalyzed molecular weight growth chemistry.

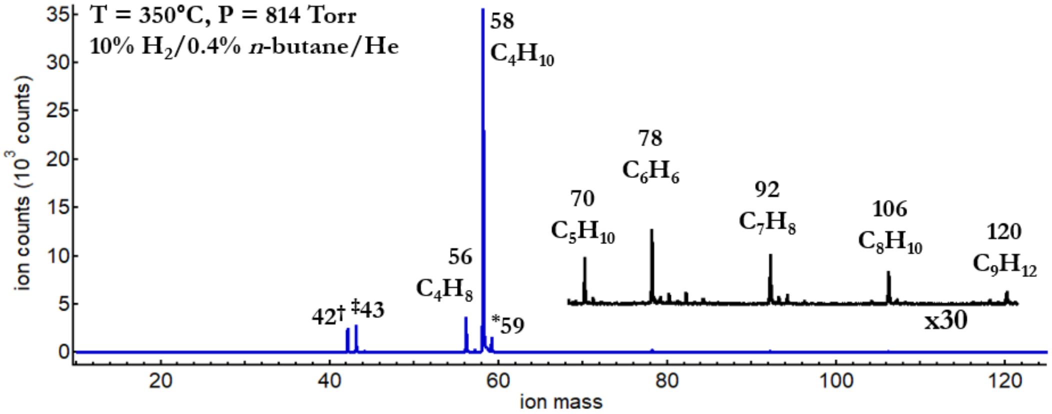

Figure 2. Typical mass spectrum of *n*-butane conversion over ZSM-5, acquired using H_2 discharge-lamp radiation at SNL. The peak at *m/z* = 58 is due to the parent ions of *n*-butane; the peaks at *m/z* = 56, 70, 78, 92, 106, and 120 are due to the products of catalytic *n*-butane conversion. * - *m/z* = 59 is due to the ^{13}C isotope of *n*-butane (natural abundance, 4.4%); ‡ - *m/z* = 43 is due to dissociative ionization (DI) of *n*-butane; † - *m/z* = 42 is mainly due to DI of *n*-butane with a small contribution from direct ionization of propene (C_3H_8)

The intensities of the key product peaks are plotted in **Figure 3** for CTR temperatures in the 100 – 350°C range. Note that these experiments were conducted with D_2 substituted for H_2 in the gas flow, resulting in extensive H/D exchange such that the products were strongly dominated by C_4D_8 (*m/z* = 64), C_5D_{10} (*m/z* = 80), C_6D_6 (*m/z* = 84), $C_7D_5H_3$ (*m/z* = 97), $C_8H_4D_6$ (*m/z* = 110), and $C_9D_3H_9$ (*m/z* = 123). The product T-dependence in **Figure 3** demonstrates that the onset of conversion of *n*-butane and isobutane is at ~250°C and 200°C, respectively.

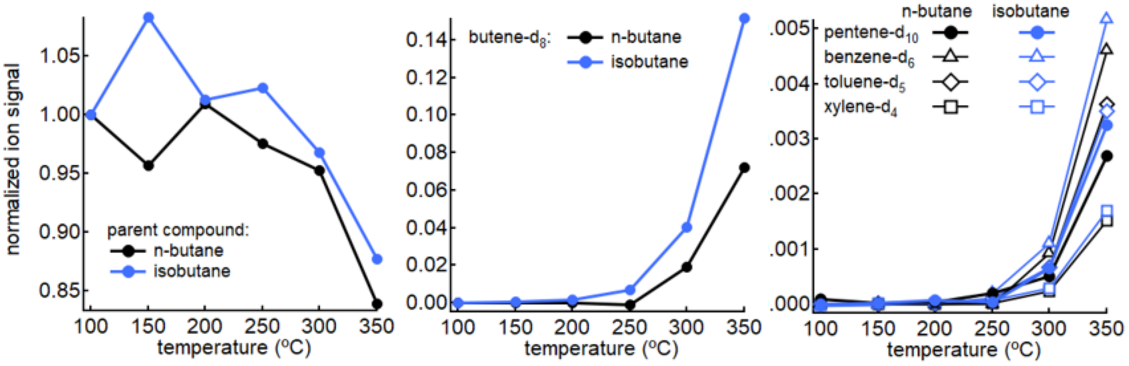

Figure 3. T-dependent ion peak intensities during *n*-butane (black) and isobutane (blue) conversion over ZSM-5, relative to the parent compound at T = 100°C. The gas flows were 10% D_2/0.4% C_4H_{10}/He. *Left*: the parent ion peak (*m/z* = 58); *middle*: the main product, butene-d_8 (*m/z* = 64); *right*: the main C_5 product channel (C_5D_{10}, *m/z* = 80) and aromatic products C_6D_6, $C_7D_5H_3$, and $C_8D_4H_6$ (*m/z* = 84, 97, and 110, respectively).

The H/D exchange dynamics were studied in real-time by taking mass spectra with 40-second averaging at each time point, as shown for *n*-butane in **Figure 4** (for *m/z* = 2 – 4 and 54 – 65 amu regions). Initially, only the H_2 peak (*m/z* = 2), the *n*-butane peaks (*m/z* = 58 and 59), and the main product peak (butene, *m/z* = 56) are visible. At time point 12 we switched the H_2 abruptly for D_2. The *m/z* = 2 ion peak was replaced by a peak at *m/z* = 4 within 2 time points (~80 s), indicating that D_2 fully replaced H_2 in the bulk gas within that time. During this period the HD ion peak at *m/z* = 3 appeared and decayed below the noise level – proof that H_2 and D_2 undergo dissociative adsorption to the catalyst or CTR walls, followed by recombination to HD, and desorption. In contrast, the C_4H_8 peak disappeared quickly but was *gradually* replaced by progressively more highly D-substituted products until C_4D_8 (*m/z* = 64) became dominant at time point 20. This suggests that H/D exchange reactions with C_4H_8 took place not in the gas phase or on the CTR walls, but rather mainly inside the catalyst pores, in which the change from H_2 to D_2 gas was slow. Moreover, *n*-butane did not undergo H/D exchange at all. At time point 52 the D_2 flow was switched back to H_2 and the changes to the mass spectrum were reversed on the same timescale.

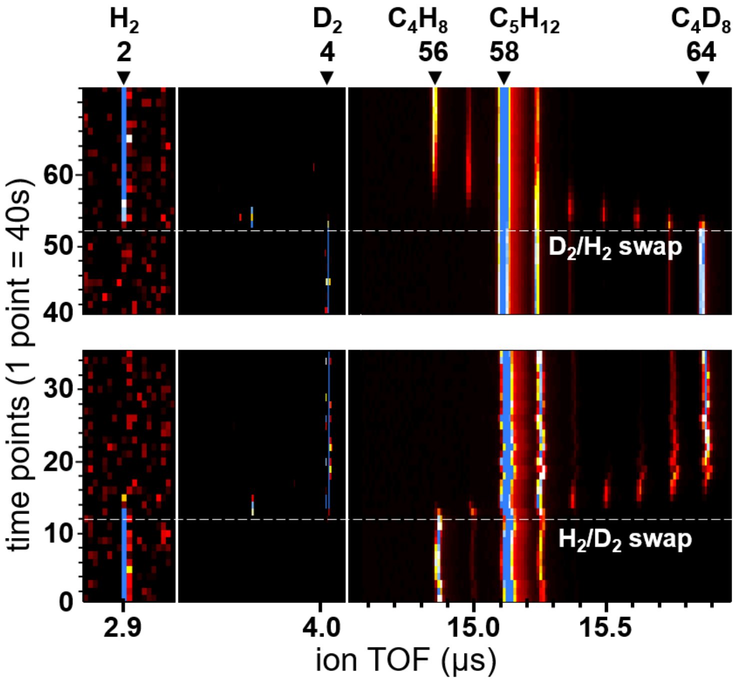

Figure 4. Time-resolved mass spectrum of H/D atom exchange in *n*-butane conversion over unmodified ZSM-5 zeolites, acquired with 40 s integration time for each time point. Initial conditions are the same as in Fig. 2 (T = 350°C, P = 800 Torr, 10%H_2/0.4% *n*-butane/He); at time point #12 the H_2 flow is replaced by an equivalent flow of D_2; at time point #52 the D_2 flow is replaced by H_2.

In summary, the results of **Figure 4** thus provide some important insights into the catalytic activity of ZSM-5 in our experiments:

- The H/D exchange with butane conversion products occurs mainly in the catalyst pores.
- The H/D exchange happens only to hydrocarbons that are reacting on the surface and not to the butane molecules that may adsorb and desorb without reacting.
- Dissociative adsorption of H_2/D_2 and the H/D exchange with adsorbed hydrocarbons is fast, compared to the mixing of carrier gas in the ZSM-5 pores. The degree of D substitution in the detected products therefore reflects the H/D surface coverage at any instant, which itself reflects the slow change of the carrier gas in the pores.

The H/D exchange patterns of the aromatic products ($C_6H_6 \rightarrow C_6D_6$, $C_7H_8 \rightarrow C_7D_5H_3$, $C_8H_{10} \rightarrow C_8H_4D_6$, $C_9H_{12} \rightarrow C_9D_3H_9$) imply that these compounds contain 6, 5, 4, and 3 equivalent H atoms that undergo the exchange, respectively. These patterns point to specific product isomer assignments, even though these experiments did not employ tunable VUV radiation that would enable resolution of isomers from PI spectra. For example, the four D atoms at mass 110 imply that the $m/z = 106$ peak is due to a xylene, $C_6H_4(CH_3)_2$, which has four equivalent aromatic and six equivalent methyl C-H bonds. It is inconsistent with ethylbenzene, $C_6H_5CH_2CH_3$, which has five equivalent aromatic C-H, as well as two secondary and three primary aliphatic C-H bonds. Similarly, the three D atoms at $m/z = 123$ are consistent only with trimethylbenzene ($C_6D_3(CH_3)_3$), rather with other possible isomers. The number of D atoms at $m/z = 97$ and 84 are consistent only with toluene ($C_6D_5CH_3$) and benzene (C_6D_6), respectively. Our assignment of the aromatic products is shown in **Figure 5**,

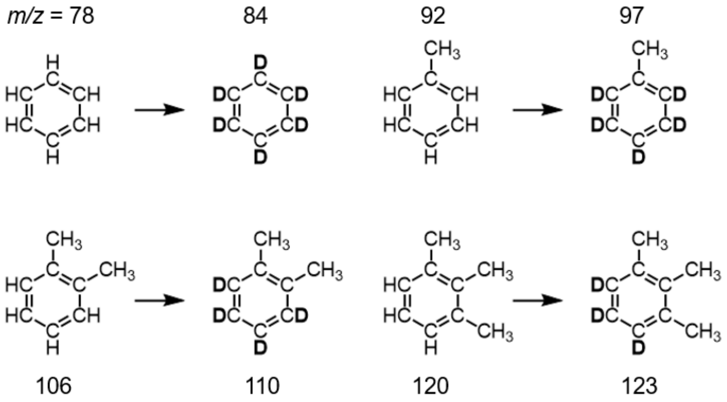

Figure 5. Proposed assignment and H/D exchange patterns of the observed ion peaks in the $C_6 – C_9$ range. Note that for clarity we only show one of the 3 possible isomers (o-, m-, p-xylene) for the C_8H_{10} peak and one of the 3 possible isomers (1,2,3-, 1,2,4-, and 1,3,5-trimethyl benzene) for the C_9H_{12} peak.

Furthermore, these results suggest that only the aromatic H atoms undergo H/D exchange, whereas methyl H atoms do not. This is a fascinating finding because in the gas phase the methyl C-H bonds in CH_3-substituted aromatic hydrocarbons are nearly 100 kJ/mol weaker than aromatic C-H bonds. Understanding this remarkable selectivity of zeolite-catalyzed H/D exchange for aromatic H atoms would undoubtedly bring valuable mechanistic insight.

We also conducted studies of *n*-butane and isobutane conversion over ZSM-5 at the ALS. A typical mass spectrum from *n*-butane experiments, integrated over VUV photon energies 8.8 – 10.4 eV, is shown in **Figure 6**. In addition to observing the same ion peaks as discussed above, we also detected very small signals at $m/z = 15$ (CH_3). The photoionization spectrum of this small peak from isobutane experiments is plotted in **Figure 7** (left panel) and matches quite well the published PI spectrum of the methyl radical.[17, 18] The spectrum from *n*-butane experiments is similar. This PI spectrum is unambiguous confirmation that CH_3 radicals are produced from zeolite-catalyzed conversion of both model compounds and desorbed into the gas phase.

The energy-resolved PIMS experiments at the ALS enabled the quantification of chemical isomers that contribute to the major C_4H_8 products of *n*-butane and isobutane conversion. As an example, we show the analysis of the $m/z = 56$ PI spectrum from isobutane experiments in **Figure 7** (right panel). The spectrum is fit to the sum of isobutene and 1-butene spectra with negligible contribution from 2-butene. **Figure 8** presents the relative mole fractions of methyl, propene, and butene isomers from isobutane and *n*-butane experiments, confirming that butene is the main products of *n*-butane and isobutane, with smaller (factor of 3 – 8) yields of propene and significantly smaller (factor of ~100) yields of methyl detected in the gas phase. The PI spectrum analysis of other minor products was not feasible due to numerous isomers and low signal levels.

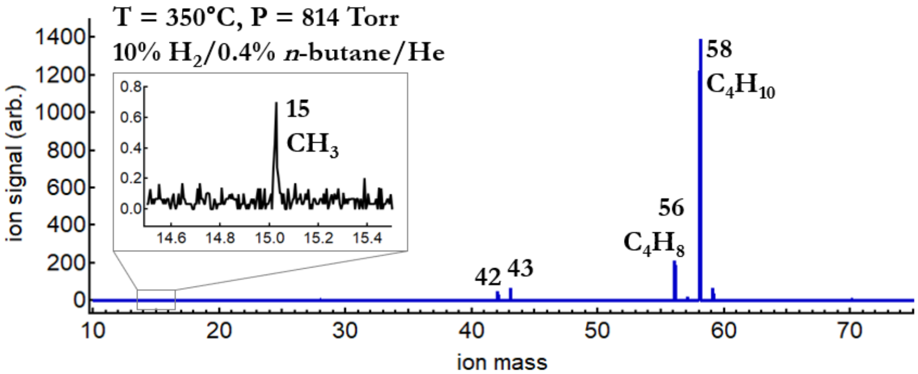

Figure 6.Mass spectrum of *n*-butane conversion over unmodified ZSM-5 zeolites, acquired at the ALS and integrated over VUV photon energies 8.8 – 10.5 eV. The main peak assignments are the same as in Fig. 2. A small ion peak at $m/z = 15$ is assigned to methyl radical, CH_3.

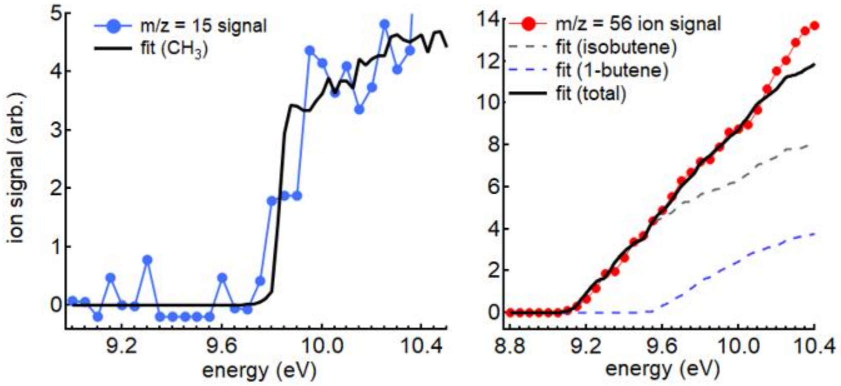

Figure 7. PI spectra of *m/z* = 15 (*left*) and 56 (*right*) ions, collected during the catalytic conversion of isobutane over ZSM-5 (18% H_2/0.9% isobutane/He, T = 250°C, P = 820 Torr). The left panel shows a fit to the reference PIXS of methyl radical (CH_3). The right panel shows a combined fit and the individual contributions of the reference PIXS of 1-butene (blue) and isobutene (gray).

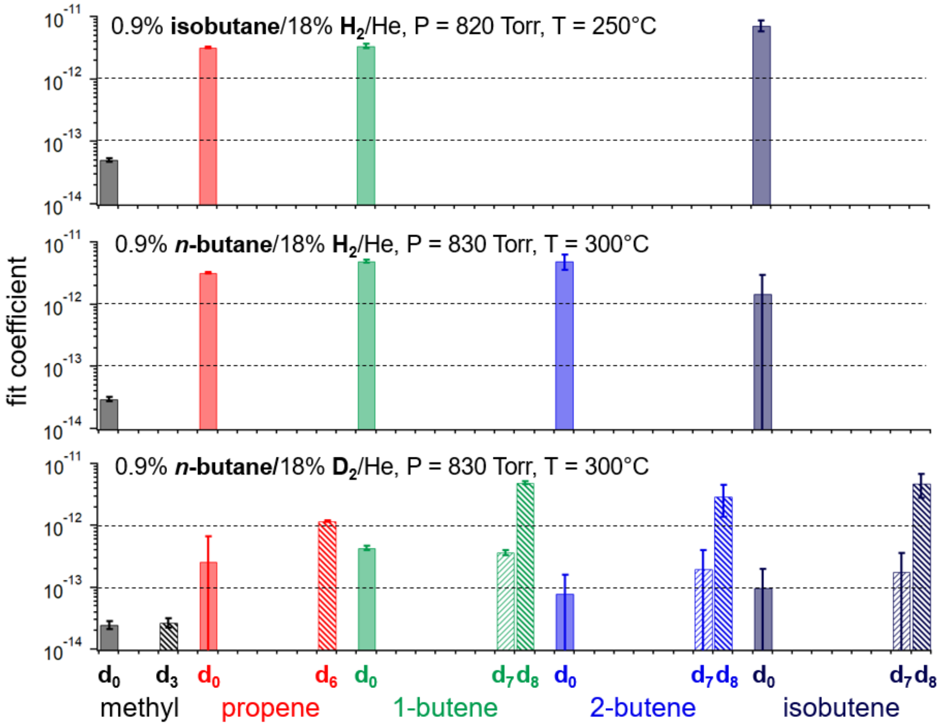

Figure 8. Product distributions measured during the catalytic conversion of *n*-butane and isobutane over ZSM-5. The plotted fit coefficients are proportional to the relative molar fraction of each chemical species in the gas phase, sampled into the mass spectrometer.

Figure 8 reveals the formation of a branched product isobutene from unbranched *n*-butane and linear C_4 product 1-butene from branched isobutane. These results provide strong evidence that CH_3 radicals participate in the catalytic chemistry, consistent with our direct detection of methyl. It is also notable that no 2-butene isomers are detected from isobutane, suggesting selectivity in the methylation reactions. We present a possible explanation for this observation in **Figure 9**. If the resonance-stabilized allyl radical (C_3H_5) were the intermediate in methylation, as is shown in **Figure 9**, this reaction would only proceed by CH_3 addition to the terminal C atom of allyl, forming only 1-butene. The addition of methyl to the central C atom would produce a biradical and would thus be energetically unfavorable. Although speculative, this explanation exemplifies the mechanistic insight that may be afforded by our detailed chemical speciation measurement and provides motivation for further research.

Furthermore, the observation in **Figure 8** of either undeuterated or essentially fully deuterated products when D_2 is used with d_0-*n*-butane is surprising. Although we have no full explanation for these observations, they may imply two distinct mechanism for production of alkenes. One mechanism may be more direct, leading to no D atom substitution, whereas the competing, dominant mechanism must involve complete accommodation of the reactant with the surface, leading to complete (or nearly complete) D-atom substitution. These clues add to the promise of our experimental technique for fundamental mechanism discovery.

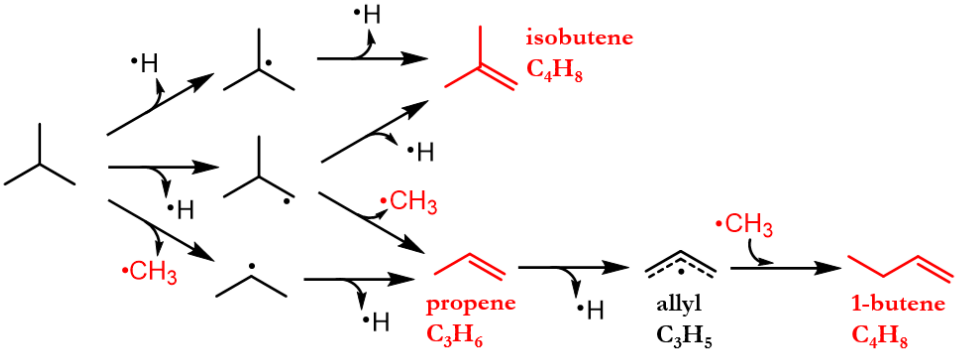

Figure 9. Proposed partial reaction scheme for the catalytic conversion of isobutene over ZSM-5 zeolites. The chemical structures and formulae marked in red have been experimentally detected here.

Complex HDPE depolymerization chemistry over Ir-ZSM-5 catalyst

Our second goal via test case #2 was to assess whether PIMS measurements can elucidate key pathways in the depolymerization of HDPE, a common everyday plastic. Recovery of valuable products from HDPE recycling is complicated by low selectivity of depolymerization due to the very large number of identical -CH_2- groups that comprise HDPE chains. However, the group of Prof. Chao Wang at Johns Hopkins University has developed an Ir-modified ZSM-5 catalyst that may offer high selectivity and provided us this catalyst to test our methodology. Like our model compound studies, we paired survey experiments at Sandia over a broad range of conditions with targeted speciation measurements at the ALS. We placed small (~0.01 cm^3) samples of HDPE, embedded with Ir-ZSM-5 powder, into the CTR and flowed carrier gas (5 – 30% H_2 in balance He, total P ~ 800 Torr) over them. We found that the samples melted above 200°C and bubbled uncontrollably at 350°C, which degraded the CTR operation and clogged the sampling nozzle. Consequently, we limited our temperatures to below 320°C for most experiments.

Figure 10 plots a mass spectrum, collected at 300°C at the ALS over VUV energies 9 – 11.5 eV. It shows a strong peak progression of alkenes (C_nH_{2n}, n = 2 – 26, dominated by n = 3 – 6), and a second peak progression due to alkanes (C_nH_{2n+2}, n = 3 – 26). Heavier compounds may be present but are not detected above the experimental noise level. In addition, aromatic compounds $C_6H_6(CH_2)_n$, n = 1 – 4, were detected. Based on the analogy with model compounds, described above, we assign these peaks to toluene ($C_6H_5CH_3$) and methyl- or possibly ethyl-substituted benzene isomers. At lower T, we also observed benzene, C_6H_6. We did not determine the isomer distributions of the C_8 – C_{10} aromatics because their literature PIXS were similar to each other or not known. These compounds were minor products and we did not explore their yields further.

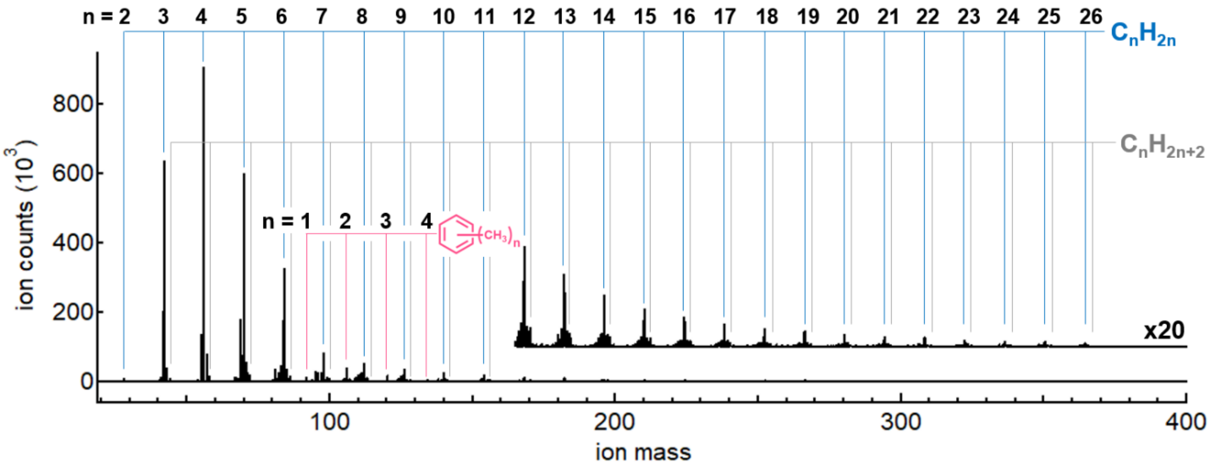

Figure 10. Mass spectrum (integrated over VUV energies 9 – 11.5 eV) collected during depolymerization of HDPE over Ir-ZSM-5 at T = 300°C, P = 830 Torr (5%H_2/He). Ion peaks due to parent ions of alkenes (C_nH_{2n}, n = 2 – 26), alkanes (C_nH_{2n+2}, n = 3 – 26), and $(CH_3)_n$-substituted benzene (n = 1 – 4) are marked; the remaining peaks were assigned to DI fragments of alkenes and alkanes.

Numerous other peaks were observed in the mass spectra, particularly in the C_nH_{2n-1}, C_nH_{2n-2}, and C_nH_{2n+1} progressions. Based on their PI spectra and the known fragmentation patterns of alkane and alkene cations, we assign all of these peaks to DI fragments of the main alkene and alkene products (specifically, the loss of neutral H, CH_3, CH_4, and C_mH_{2m-1} fragments).

We tested the dependence of the mass spectra on experimental conditions and found that varying H_2 between 5 - 30% of the total carrier gas flow had minimal impact on the observed product distributions. T-dependent mass spectra are shown in **Figure 11** along with quantified T-dependent intensities of select product signals, demonstrated strong increase in depolymerization activity with increasing T. Note that although the ion signals in **Figure 11** are not equivalent to molar fractions, we conclude qualitatively that light alkene yields increase monotonically with temperature, whereas the yields of C_7 and heavier alkenes begin to decrease in going from 280°C to 300°C. In contrast, all alkane and aromatic product peaks continue to increase at 300°C. This trend was confirmed by Sandia experiments that went up to 320° C. Lastly, we explored different average gas residence times in the CTR (0.04 – 0.3 s) and found that all peak signals scaled proportionately to the residence time. This result suggests that the volatile depolymerization products were simply diluted more by larger carrier gas flows at shorter residence times.

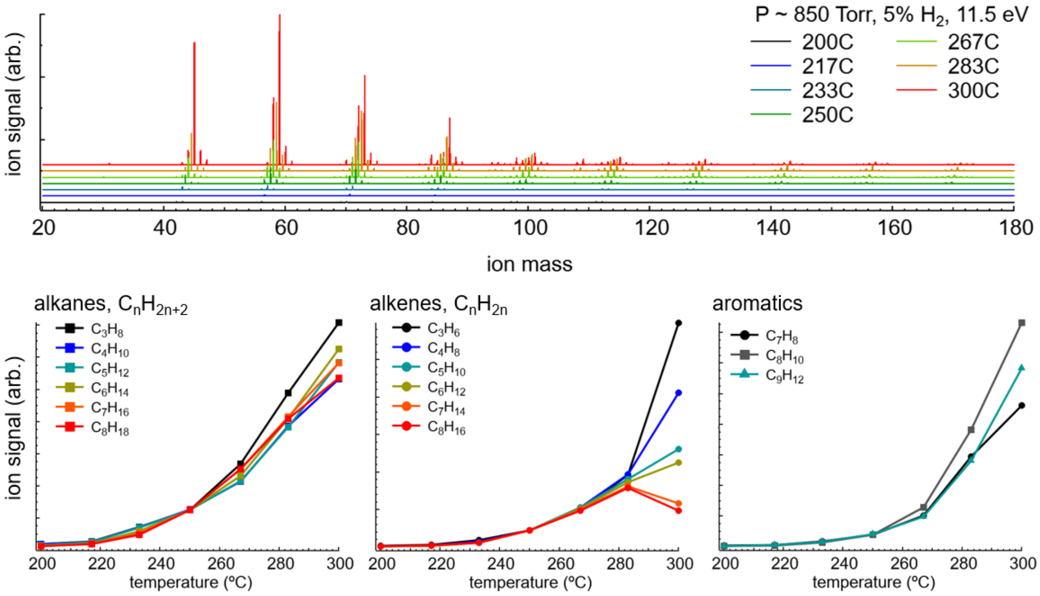

Figure 11. *Top*: T-dependent mass spectra, taken at 11.5 eV during HDPE depolymerization over Ir-ZSM-5 under ~850 Torr total pressure (5%H_2/95%He). Only the mass region m/z = 20 – 180 is shown for clarity. *Bottom*: T-dependent signals of the main ion peaks due to alkanes, alkenes, and aromatics (in each case scaled for comparison so that the peak intensities at 250°C are equal).

We conducted several experiments at the ALS in which D_2 was substituted for H_2 at otherwise identical CTR conditions. Representative molar fractions of select $C_2 – C_4$ product isomers, discovered in these experiments, are plotted in **Figure 12**. The reference PIXS of isobutene and 2-butene are similar and the signal-to-noise level of the data was too low to be confident in their quantification; hence we plot the sum of isobutene and 2-butene molar fractions, which is a reliable quantity. The results in **Figure 12** show that H/D exchange under steady-state conditions was minor, in stark contrast with the results from model compound experiments in **Figure 8**. The ethene, propene, and butene peak distributions are remarkably consistent, with ~80% in the d_0 peak, 12 - 16% in the d_1 peak, ~2% in the d_2 peak, and <1% in all other peaks. For propane, we found ~60% of the products to be propane-d_0 and the remaining 40% were approximately evenly split among the $d_1 – d_8$ peaks. These results suggest that unlike the pure gas/solid environment of the model compound studies, the HDPE/Ir-ZSM-5 melt limits the influence of the gas phase. The H atoms that participate in the depolymerization reactions (e.g., to form shorter alkanes) likely come mostly from the polymer molecules rather than the carrier gas.

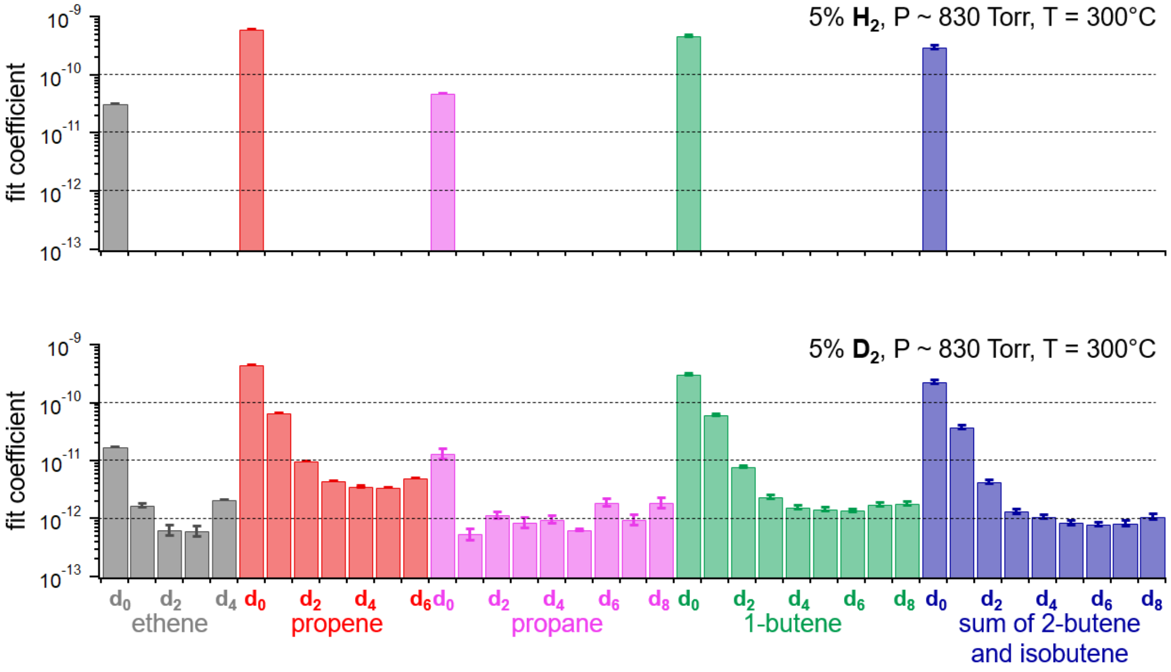

Figure 12. Product distributions of select isomers discovered during the depolymerization of HDPE over Ir-ZSM-5 under 5% H_2/He (top) and 5% D_2/He (bottom) atmosphere. The plotted fit coefficients are proportional to the relative molar fraction of each chemical species in the gas phase, sampled into the mass spectrometer.

We performed a quantitative speciation analysis on all ion peaks for which we had available reference PIXS: C_2 – C_5 alkenes and C_3 – C_6 alkanes. The possible number of chemical isomers grows rapidly with molecular size, going from one for n = 2 – 3 to 20 for n = 6. We used the available literature PIXS and independently measured the missing reference PIXS up to C_6 alkanes but did not have the resources to do so for the 13 possible C_6 alkene (C_6H_{12}) isomers. The resulting product distribution is shown in **Figure 13**, with product molar fractions expressed relative to that of the most abundant species, propene. Follow-up experiments at the same reactor conditions reproduced the PI spectra of all ion peaks within measurement uncertainty, supporting the reliability of our measurements.

We found that many species have somewhat similar PI spectra and the quality of their literature PIXS was not sufficient to confidently estimate their molar fractions. In the future, this difficulty can be solved by collecting better reference PIXS with higher spectral resolution (<20 meV) and better signal averaging. At present, we can only report the upper-limit yields of some possible product isomers; fortunately, those species are not the dominant contributions at their *m/z* ratio.

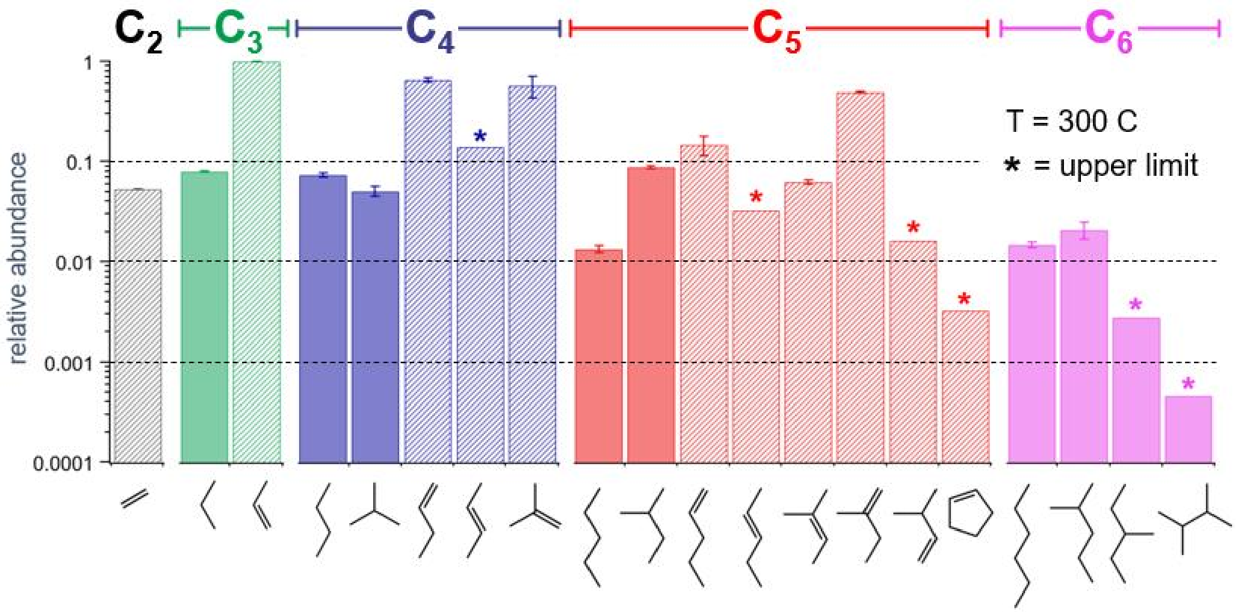

Figure 13. Product distributions of select C_2 – C_6 isomers discovered during the depolymerization of HDPE over Ir-modified ZSM-5 zeolites under 5% H_2/He atmosphere at total P = 830 Torr, T = 300°C. The molar fractions of each chemical species, sampled from the gas phase, are plotted relative to that of propene (C_3H_6). The molar fractions marked by and asterisk are upper limits only.

The main results of this analysis are summarized as follows:

- The product distributions are very broad and include numerous branched alkanes and alkenes, suggesting significant methylation chemistry.
- The yields of C_4H_8 and C_5H_{10} alkenes with terminal C=C double bonds are more than ten times higher than of those with internal C=C bonds, suggesting selectivity of the depolymerization mechanism. (For C_2 and C_3 alkenes no internal C=C bonds are possible).
- The yields of branched alkenes are high, for which there is no unifying explanation based on the radical chain mechanism.

ANTICIPATED OUTCOMES AND IMPACTS:

This project was our first foray into relatively unexplored territory – detailed mechanistic studies of catalytic (de)polymerization – and our main goal was to assess the promise of a new experimental approach. Because of this, the outcomes and impact of this projects are mostly forward looking and center on potential new research programs that can be based on the results discussed above.

Notable new results

Although our results are preliminary, they contain several notable achievements, including:

- The first direct detection of a radical intermediate (CH_3) in a depolymerization reaction.
- Determination of branched hydrocarbon products as evidence of methylation chemistry.
- Discovery of unexpected selectivity in isobutane conversion over ZSM-5 catalyst to isobutene and 1-butene, but not 2-butene.
- Discovery of selectivity in HDPE deconstruction towards terminal alkenes.
- Discovery of surprising H/D exchange dynamics in aromatic hydrocarbon products.

These results provide critical validation of our experimental approach and show its potential for fundamental mechanism discovery. We plan to discuss the path forward, including possible additional studies that are required to support and expand on the existing results, with our external scientific collaborators (Prof. Chao Wang, Johns Hopkins and Prof. Ambar Kulkarni, UC-Davis).

Scientific impact

This project demonstrated that PIMS measurements of the gas phase can provide valuable information on the chemical and physical processes in a complex multiphase reaction system significantly faster and with higher degree of chemical speciation than by other widely used analytical methods. This approach opens the door to discovery and validation of chemical mechanisms of (de)polymerization in unprecedented detail. With additional improvements to the experimental setup (and if combined with theoretical studies), our approach may probe networks of catalytic reaction to the level of individual elementary steps and microcanonical reaction rate coefficients.

If successful, these developments may lead to functionally complete understanding of (de)polymerization mechanisms. Such knowledge could inform chemical upcycling approaches for today's plastics. In the longer term, it could accelerate rational co-design of new polymers, catalysts, and processes of a circular recycling economy, facilitating chemical upcycling of new polymers and the efficient use of energy and materials.

Staff development and program impact

The leadership of center 8300 has developed a strategy of increasing cross-cutting scientific collaborations within Sandia and with outside institutions. As part of that strategy, all members of our team have participated in a lab-wide reading group focused on Chemical Upcycling of Polymers (led by Sheps) and in developing research proposals aimed at polymer upcycling. These activities bring together researchers with diverse areas of expertise. The Exploratory Express LDRD funds under this project have furthered this strategy providing our team with experience in working directly with polymers and studying the relevant scientific literature.

Potential new research and development

In 2019 – 2021 the DOE has signaled through its reports, advisory committees, and other communications, that polymer upcycling will be a major new research direction under multiple offices. In addition to holding its 2019 Polymer Upcycling Roundtable, DOE has announced a Plastics Innovation Challenge (PIC), which aligns the relevant activities within its Offices of Science, Energy Efficiency and Renewable Energy, Fossil Energy, and Advanced Research Projects Agency – Energy. Through the PIC, DOE has set out ambitious goals for 2030 and has sought input from stakeholders via a request for information, to which Sandia responded in March 2021. In January 2021 DOE/BES has issued a funding call in chemical upcycling of polymers, and we anticipate a similar call in early 2022. Based on the results reported here, we plan to pursue new research opportunities as follows:

- We will develop BES research proposals aimed at fundamental mechanistic understanding of polymer upcycling chemistries.
- We have engaged with 8624 staff to write a concept paper for an upcoming Advanced Manufacturing Office (AMO) funding call, focused on detailed probing of catalytic deconstruction of biopolymers.

- We will respond to other DOE funding calls, aided by the cross-discipline collaborations we developed through the Chemical Upcycling of Polymers reading group.
- We will pursue LDRD funding opportunities related to polymer upcycling, especially in the context of research foundations aimed at Climate Change, Bioscience, and Materials Sustainability.

Lessons learned

An important outcome of this project is a good understanding of the challenges and opportunities that lie ahead, rooted in the experience we gained in the first application of our experimental technique. We summarize the main lessons learned below:

- Dedicated catalytic reactors should be developed for solid/gas environments and multiphase (solid, liquid, polymer melt, and gas phase) environments.
- The solid/gas catalytic reactors should be able to hold small solid particles and powders under a wide range of gas flow speeds without clogging the sampling nozzle or the pumping ports. This reactor will be most useful for fundamental reactivity studies on simplified model compounds.
- The multiphase reactor should handle viscous or liquid samples without bubbling or spilling over. The carrier gas flow should be optimized to most efficiently entrain volatile products from the solid, liquid, or melt.
- A library of high-quality reference PI spectra should be compiled for relevant alkanes, alkenes, and aromatic molecules. Ideally, these reference spectra should be obtained on the same PIMS apparatus used for the catalytic depolymerization studies to minimize instrument-dependent systematic errors.

The recommendations listed above will strengthen our future proposals and accelerate future research.

CONCLUSION:

We presented a proof-of-principle demonstration of a new experimental methodology, using advanced photoionization mass spectrometry for detailed chemical analysis of the gas phase in catalytic depolymerization of HDPE as a test case. The goal of this approach is to improve on the current state-of-the-art experimental capabilities in catalytic (de)polymerization research. Specifically, we aim to:

- Enable sensitive detection of unstable reactive intermediates as well as final products,
- Facilitate universal, isomer-selective speciation measurements, and
- Collect rapid on-line measurements with resolution of seconds to minutes in order to probe the relevant timescales of physical and chemical processes in complex, multi-phase depolymerization reactions.

Using this approach, we investigated the depolymerization of high-density polyethylene (HDPE) over Ir-doped zeolite catalysts, provided by the group of Prof. Chao Wang (Johns Hopkins University). We showed that the product distribution was dominated by low-molecular (C_3 – C_6) weight alkenes with terminal C=C double bonds and revealed the presence of many methyl-substituted alkenes and alkanes, suggesting extensive methyl radical chemistry. We mapped out the temperature dependence of the product distribution and showed that it was relatively insensitive to the molar fraction of H_2 in the gas phase.

To bring further insight into the HDPE depolymerization mechanism, we investigated the fundamental reactivity of model oligomer molecules *n*-butane and isobutane over ZSM-5 zeolites. We demonstrated the first direct detection of methyl radical intermediates, confirming the key role of methyl in zeolite-catalyzed activation of alkanes. In addition, we observed apparent selectivity towards isobutene and 1-butene in the conversion of isobutane. We surveyed the dependence of the product distributions on reaction conditions: temperature, gas residence time, and composition of the reducing atmosphere (molar fraction of H_2 or D_2).

Our results show that rapid, chemically detailed measurements of the gas phase provide valuable information on the extensive networks of reactions that occur in the gas/solid or gas/polymer melt/solid environments. This work offers a tantalizing glimpse of the fundamental steps that underpin the rich, complex catalytic depolymerization chemistry and builds a scientific and technical foundation for future research in chemical upcycling of polymers.

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