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Catalytic *n*-pentane conversion on H-ZSM-5 at high pressure†

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The effect of temperature (633–723 K), pressure (10–60 bar) and weight hourly space velocity (WHSV) (400–1500 g_{C5} g_{cat}^{−1} h^{−1}) on the conversion of *n*-pentane on H-[Al]ZSM-5 type catalysts has been investigated. Catalyst properties were tested using a packed-bed laboratory microreactor and reaction products were analyzed via online gas chromatography. 5–25% pentane conversion was observed at a pressure of 40 bar and temperatures in the range of 633–723 K. Reactant consumption rate approached saturation kinetics at pressures above 30 bar (~14% conversion, 673 K). At 40 bar and 673 K, increasing WHSV (400–1500 g_{C5} g_{cat}^{−1} h^{−1}) resulted in a reduction in pentane conversion (26–10%). In all cases, propane and butane were the major products, followed by heavier C₆₊ compounds and other lighter products (C₁–C₄ paraffins and olefins). Propane carbon selectivity increased from 24% at 633 K to 34% at 723 K, while butane carbon selectivity (~40%) was nearly constant. An inverse relationship between the production of C₆₊ and light products was observed with changes in reaction conditions. The carbon selectivity to C₆₊ compounds increased from 20% at 10 bar to 27% at 60 bar and decreased from 28% at 633 K to 18% at 723 K. At all reaction conditions, the observed product distribution can be explained as the result of fast bimolecular reactions, including hydride transfer and alkylation.

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1. Introduction

This investigation is motivated by the need to develop more efficient cooling technologies for the practical use of new hypersonic engines. The flight of aircraft and missiles at hypersonic speeds (greater than Mach 5) is hindered by overheating of the engine and electronic components caused by the high rate of fuel combustion and air friction.¹ Aircraft are currently cooled by passive and active methods: when passive cooling is used, cold air from the atmosphere is passed through the engine, whereas when active cooling is used, onboard jet fuel is used as a heat sink.² In such cases, the maximum amount of heat that can be removed is determined by the heat capacity, thermal stability, and initial temperature of the fuel. Chemical additives (e.g. 1,2,3,4-tetrahydroquinoline and tetralin) and special fuels (e.g. *exo*-tetrahydrodicyclopentadiene) with greater heat capacity and thermal stability have been designed for this purpose, but future hypersonic vehicles will exceed the cooling capacity of these special fuels.^{3,4}

Cooling capacity can be improved by utilizing so-called endothermic fuels, which undergo endothermic chemical reactions

driven by the thermal energy removed from the aircraft^{5,6} and a target endothermic reaction is the cracking of hydrocarbons on solid catalysts. For several decades, zeolites have been used as catalysts for cracking of crude oil,^{7,8} but there are only a few reports of zeolite-based high-pressure cracking for endothermic fuel applications.^{9–12} To maximize endothermicity, the selective cracking of alkanes to produce an alkene and a smaller alkane is the preferred reaction. It is also desired to further crack the alkene and alkane to produce hydrogen, ethene, and methane, as these have better mixing and combustion characteristics than larger molecules.¹³

Zeolite catalyzed cracking of alkanes proceeds via two major mechanisms: monomolecular and bimolecular.¹⁴ Monomolecular (*i.e.* protolytic) cracking reactions typically occur at low pressures and high temperatures.^{15–21} In this mechanism, a proton from the zeolite acid site is transferred to the adsorbed alkane to form a pentacoordinated alkanium ion that immediately undergoes protolytic cracking to form a neutral paraffin or molecular hydrogen and a surface alkoxide. The surface alkoxide can desorb to produce an olefin and reform the zeolite acid site.^{22–26} This sequence leads to a predictable, but approximate, product distribution. For example, the protolytic cracking of butane can only yield three product pairs: hydrogen and butene, methane and propene, or ethane and ethene. Surface alkoxides can also undergo further cracking through β-scission reactions.

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Alkoxides may also participate in bimolecular reactions, such as hydride transfer, oligomerization, and alkylation.⁸ In bimolecular reactions, a molecule in the gas phase reacts with a chemisorbed olefin on the surface of the zeolite. The simplest way to detect bimolecular reactions is to observe molecules that cannot be formed from monomolecular cracking; for example, the production of pentane from hexane. Methane and pentene can be produced from protolytic cracking of hexane. Pentene then can be converted to pentane through hydride transfer. Pentane can also be formed by cracking larger molecules that formed through oligomerization.

There have been a few investigations of the supercritical cracking of hydrocarbons on zeolites. Dardas *et al.* investigated the effects of supercritical pressures on the conversion and selectivity of *n*-heptane cracking on Y-type zeolites. The supercritical pressures increased the conversion and paraffin yield and decreased the amount of deactivation observed when compared to subcritical pressures.⁹ Xian *et al.* studied supercritical cracking of *n*-dodecane on wall-coated H-[Al]ZSM-5 catalysts and reported that nanocrystalline catalyst particles produced higher conversions and higher selectivity to ethylene and propylene than microcrystal size particles.¹⁰ Kim *et al.* found that high pressure conversion of methylcyclohexane on H-[Al]ZSM-5 yielded higher heats of reactions as compared to H-[Al]Beta and H-[Al]Y.²⁷ Luo *et al.* have investigated the cracking of *n*-hexane on various zeolites. H-[Al]ZSM-5 exhibited a higher pressure dependency on rates and higher activation energies than H-[Al]USY, H-[Al]Mordenite, and H-[Al]Beta, but had better selectivity towards olefins and lower susceptibility to deactivation.^{11,12} In addition, the cracking of hexane on ZSM-5 exhibited monomolecular-like reaction kinetics under all pressures, but at high pressures on USY, mordenite, and zeolite beta, bimolecular reactions were the dominant reaction channels. Finally, Wang *et al.* found that heavily branched *iso*-dodecane (mainly 2,2,4,6,6-pentamethylheptane) could affect conversion of *n*-dodecane on H-[Al]ZSM-5 by acting as an inert diluent (positive) or by resisting diffusion (negative).²⁸

In this report, the effects of temperature, pressure and weight hourly space velocity (WHSV) on the conversion of *n*-pentane on H-[Al]ZSM-5 were investigated to determine the potential of this reaction/catalyst system for endothermic cooling. The solid acid zeolite H-[Al]ZSM-5 was chosen as the catalyst because it is thermally stable, readily available, and known to increase the yield of light olefins in industrial fluidized catalytic cracking units.²⁹ Pentane was selected because it is the simplest liquid hydrocarbon at STP and has a high cooling potential (pentane cracking to ethane and propylene has a heat of reaction of 1.15 MJ kg⁻¹). In addition, *n*-pentane cannot form neutral aromatic species by cyclization and dehydrogenation without molecular weight growth.³⁰ It was found that under all reaction conditions investigated, bimolecular reactions were the dominant reaction channels for the high-pressure conversion of pentane on H-[Al]ZSM-5. Smaller alkanes (C₃, C₄) with higher H/C ratios than pentane were produced, while larger species (C₆₊) with lower H/C ratios than pentane were necessarily produced to close the hydrogen and carbon balance. This group of products has lower endothermic potential than direct monomolecular cracking of the alkane.

2. Experimental section

2.1 Materials

NH₄[Al]ZSM-5 (CBV3024E) was purchased from Zeolyst International and the material was used without further treatment for the catalytic investigations. *n*-Pentane (Fisher, 99.7% purity) was used as the feed for the catalytic tests. The following gases were used for calcination and gas chromatograph operation: air (Keen, Grade 0.1), Nitrogen (Keen, Grade 5.0), Hydrogen (Keen, Grade 5.0), and Helium (Keen, Grade 5.0).

2.2 Characterization

Solid state ²⁹Si MAS NMR (99.83 MHz, 10 kHz rotational speed, 2048 scans, and 30 s relaxation delay) and ²⁷Al MAS NMR (130.29 MHz, 10 kHz rotational speed, and 512 scans) spectra of hydrated NH₄[Al]ZSM-5 were recorded with a Bruker AVIII500 NMR spectrometer. Surface area and micropore volumes (calculated using the *t*-plot method) were determined through N₂ adsorption isotherms measured using a Micromeritics ASAP 2020 instrument. The samples were pretreated at a temperature of 623 K and a reduced pressure of 0.5 Torr for 6 h to remove any adsorbed species. Powder X-ray diffraction patterns (PXRD) were measured using a Phillips X'Pert X-ray diffractometer with a CuKα source (λ = 1.542 Å). Diffraction patterns were obtained using a step size of 0.02° 2θ with 2 s counting time at each step. Diffraction patterns were measured between 5° and 50° 2θ. SEM images were taken with a JSM-7400F scanning electron microscope with an accelerating voltage of 3.00 kV. Zeolite chemical compositions were determined through inductively coupled plasma mass spectrometry (ICP-MS) from Galbraith Laboratories, Inc.

2.3 Reactor system

Fig. 1 depicts the configuration of the experimental setup used for high-pressure experiments. The reactant, *n*-pentane, was contained in a pressurized tank (1 L); this limited amount constrained the time on stream to under 9 h. Pentane was fed

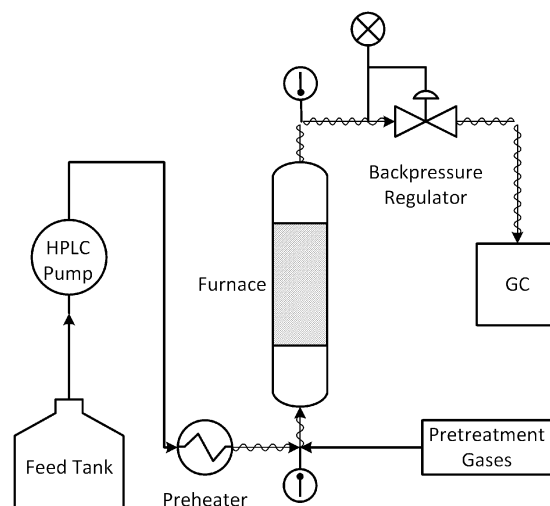


Fig. 1 Process flow diagram of the experimental setup used for high pressure experiments.

into the system using a high-pressure liquid chromatography (HPLC) pump (Chromtech, Series I). The system pressure was controlled by a backpressure regulator (Swagelok, KPB series). The reactor consisted of the catalyst supported by quartz wool inside a 316 SS tube (4.6 mm ID). Two thermocouples were installed, one at the bottom and one at the top of the catalyst bed, to monitor the temperature difference across the bed; the thermocouples also helped maintain the position of the bed within the reactor tube. A preheater (coiled 1/8" tube wrapped with heating tape) and tubular furnace (Lindberg Blue M) were used to control the reaction temperature. Gas transfer lines were heated to 453 K using heating tape to avoid condensation of products. The reactor effluent was analyzed using an online gas chromatograph (GC) (Agilent 7890B) equipped with a flame ionization detector (FID). Separation of chemical species within the reactor effluent was performed in the GC with an Alumina column (Agilent, 50 m \times 530 μ m ID). Helium was used as the carrier gas and nitrogen was used as the makeup gas. The following temperature program was used for product detection: a 5 minute hold at 373 K, a ramp to 473 K at a rate of 20 K min⁻¹, and a final 30 min hold at 473 K.

2.4 Catalytic tests

The catalyst powder was pressed, gently crushed and sieved to particle sizes between 250 and 425 μ m (40–60 mesh). Each experiment was performed using 50 mg of catalyst powder. Prior to each experiment, the catalyst was calcined *in situ* at a temperature of 823 K for 5 hours in zero air (Keen, 60 mL min⁻¹). A variety of reaction conditions were investigated: pressure was investigated up to 60 bar and reaction temperature was studied in the range of 633–723 K. Most experiments were performed in the supercritical regime of *n*-pentane (t_c = 470 K and p_c = 34 bar).³¹ The weight hourly space velocity (WHSV, defined as grams of pentane fed per gram of catalyst per hour) ranged from 375–1500 g_{C5} g_{cat}⁻¹ h⁻¹ and was controlled by changing the pentane liquid flow rates in the range of 0.5–2.0 mL min⁻¹. Conversion of *n*-pentane was defined as 100% minus the percentage of unreacted pentane (all isomers included) in the product stream. Product carbon selectivity was defined as the fraction of carbon in each product as compared to the total amount of carbon in the effluent that was not pentane.

3. Results

The conversion of *n*-pentane over zeolite H-[Al]ZSM-5 (Si/Al = 15) was investigated considering the effect of temperature (633–723 K), pressure (10–60 bar), and weight hourly space velocity (WHSV) (375–1500 g_{C5} g_{cat}⁻¹ h⁻¹). The reaction kinetics were measured using a packed-bed laboratory microreactor and reaction products were analyzed *via* online gas chromatography.

3.1 Catalyst characterization

The XRD patterns of the zeolite samples showed that the zeolite samples were highly crystalline and did not reveal the presence of any amorphous material or other crystalline impurities.

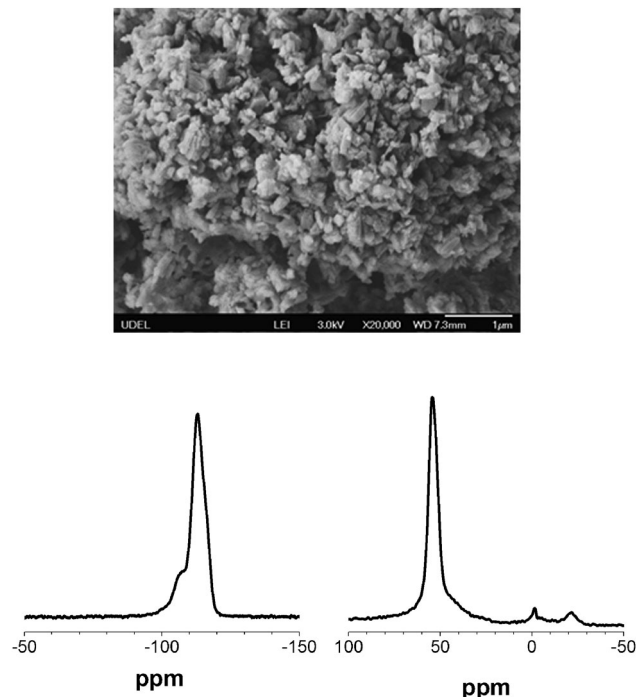


Fig. 2 SEM image of CBV3024E (top), ²⁹Si NMR (left), and ²⁷Al NMR (right) of the ZSM-5 catalyst.

The SEM image (Fig. 2) shows that the material was an aggregate of particles smaller than 2 μ m. Presence of only one signal at 55 ppm on the ²⁷Al MAS NMR spectra of the hydrated samples showed that nearly all aluminum atoms were in tetrahedral coordination (Fig. 2). Only a small fraction (1%) was observed near 0 ppm and was assigned to extra-framework octahedral aluminum. The nominal Si/Al ratio of this commercial sample determined by ICP (Si/Al = 15.7) was consistent with the aluminum concentrations determined by other studies on similar samples (Si/Al = 15–17).^{15,32} ²⁹Si MAS NMR spectra from this sample indicated that the sample contained predominantly Si(4Si) groups and 4.2% of Si(3Si, Al), resulting in an estimated framework Si/Al of 23. The aluminum concentration is slightly less than the amount observed by ICP, and confirms that only a small fraction of the Al is located in extra-framework positions.

The micropore volume, obtained from N₂ adsorption isotherms and analyzed using the *t*-plot method, was 0.11 cm³ g⁻¹. This micropore volume is slightly smaller than observed for high quality samples (usually \sim 0.14 cm³ g⁻¹) and suggest that some extra-framework species may be present in the zeolite pores or that a non-porous phase (undetected by XRD) is present in the sample. The observed BET surface area (380 m² g⁻¹) and micropore volume are in agreement with previous reports for the same material.³²

3.2 Catalytic conversion of *n*-pentane

Conversion of *n*-pentane on H-[Al]ZSM-5 at high pressures was performed in a packed-bed reactor. Reactor effluent was analyzed *via* an online GC with injections being taken approximately every 40 min. As seen in Fig. 3, reactor conversion remained stable during the 6 h of time on stream at temperatures up to 673 K.

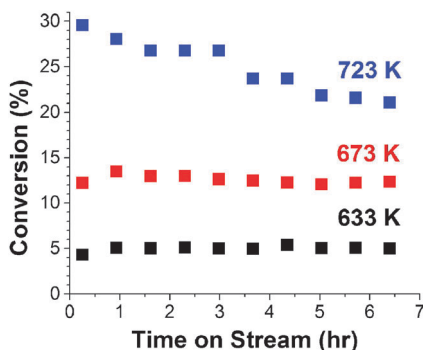


Fig. 3 Conversion of *n*-pentane over 6.5 h time on stream during high pressure conversion on H-[Al]ZSM-5. Reaction conditions: $T = 633\text{--}723\text{ K}$, $P = 40\text{ bar}$, and $\text{WHSV} = 1120\text{ g}_{\text{C}_5}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$.

Deactivation was observed at temperatures above 673 K, with the greatest amount at the highest reaction temperature of 723 K. Conversion and selectivity data were calculated from the average of the GC measurements over the 6.5 h time on stream.

Fig. 4 shows the conversion of *n*-pentane and product carbon selectivity at temperatures between 633 K and 723 K ($P = 40\text{ bar}$ and WHSV of $1120\text{ g}_{\text{C}_5}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$). Conversion increased rapidly with increasing temperature. The major products of the reaction were propane and butane ($\sim 6:4$ *n*:*iso* isomeric ratio). At all experimental conditions investigated, the selectivity to methane, ethane, ethene, propene and butenes was low ($<10\%$), hence these fractions were combined and reported as 'lights'. This fraction never exceeded 10% of the overall carbon in the product stream. A typical carbon composition of the lights was 1% methane, 5–10% ethane, 4–8% ethylene, 20–30% propylene, and 50–70% butenes. As temperature increased, selectivity to propane increased, while selectivity to butane remained nearly constant. On the other hand, selectivity to higher molecular weight products (C_{6+}) decreased with increasing temperature. A small ($<2\%$) increase in selectivity to light products was observed with increasing temperature.

Clear changes in conversion and carbon selectivity were observed as the pressure was increased at a temperature of 673 K and $\text{WHSV} = 1120\text{ g}_{\text{C}_5}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$. Increasing the pressure

of the system from 10 bar up to a total pressure of 30 bar, which is before the transition to the supercritical phase (34 bar), caused an increase in conversion. Further increases in pressure up to 60 bar did not increase the total conversion of pentane. Pressure changes had little effect on carbon selectivity of the major products: propane and butane. Conversely, increases in pressure decreased selectivity to the light products and increased selectivity to the C_{6+} fraction (Fig. 5).

Fig. 6 shows the conversion and carbon selectivity during the *n*-pentane reaction at a temperature of 673 K and a pressure of 40 bar as a function of WHSV ($375\text{--}1500\text{ g}_{\text{C}_5}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$). Conversion of pentane increased with decreasing WHSV, or in other words, increased as the residence time increased. Selectivity of the major products (propane and butane) and C_{6+} fraction did not change appreciably with changes in WHSV, but carbon selectivity of the light products increased with increasing WHSV.

4. Discussion

The formation of more than 50 different species upon the reaction of *n*-pentane on H-[Al]ZSM-5, including many compounds heavier than pentane, is clear evidence of secondary bimolecular reactions controlling the product distribution at high pressure. In addition, the ratios of C_3/C_2 and C_4/C_1 products were greater than 1 under all conditions, which further indicates a role of bimolecular reactions in the catalyst. If monomolecular cracking were occurring, the average H/C ratio of the cracked products would equal that of the feed (*n*-pentane $\text{H/C} = 2.4$), while the average H/C of products lighter than pentane was between 2.5–2.6. Since the observed $\text{C}_1\text{--C}_5$ species had an average H/C greater than the feed, either the olefins produced from monomolecular cracking were consumed in secondary reactions or the paraffins were produced *via* a reaction other than *n*-pentane cracking.

The consumption of olefins lighter than pentane through secondary bimolecular reactions is consistent with changes in the carbon selectivity of the light olefins: ethene, propene, and butene (Fig. 7). Carbon selectivity of the light olefins decreased with increasing pressure, with the change being most clear at pressures below $\sim 30\text{ bar}$, where pentane is gas-like. Although pentane

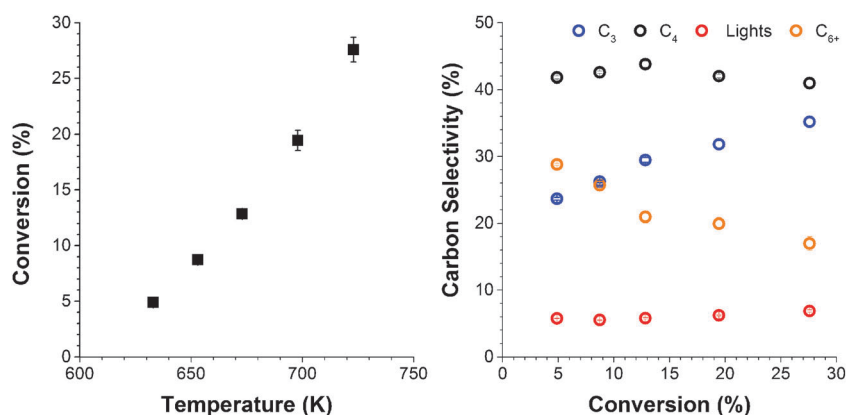


Fig. 4 Conversion of *n*-pentane (left) and selectivity to product groups (right) during high pressure conversion on H-[Al]ZSM-5. Reaction conditions: $T = 633\text{--}723\text{ K}$, $P = 40\text{ bar}$, and $\text{WHSV} = 1120\text{ g}_{\text{C}_5}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$.

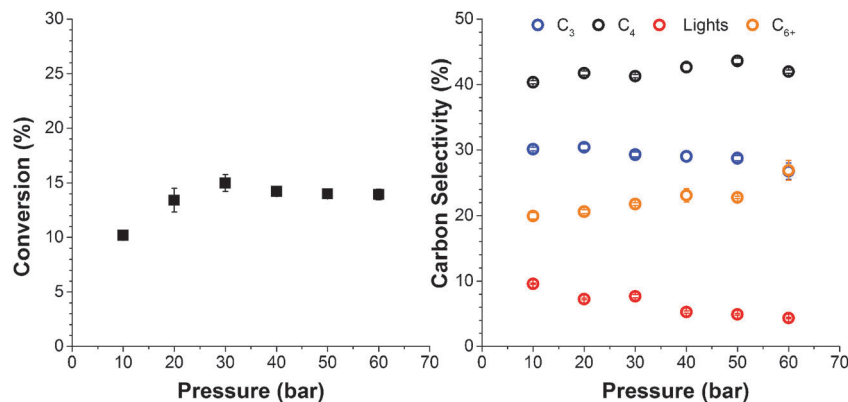


Fig. 5 Conversion of *n*-pentane (left) and selectivity to product groups (right) during high pressure conversion on H-[Al]ZSM-5. Reaction conditions: $T = 673\text{ K}$, $P = 10\text{--}60\text{ bar}$, and $\text{WHSV} = 1120\text{ g}_{\text{C}_5}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$.

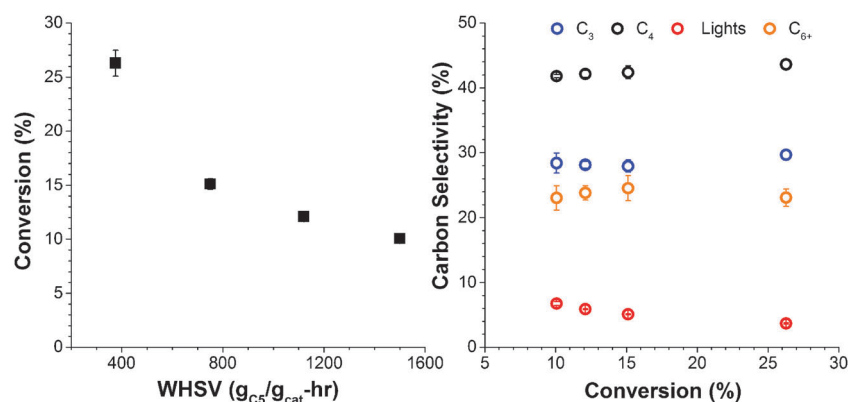


Fig. 6 Conversion of *n*-pentane (left) and selectivity to product groups (right) during high pressure conversion on H-[Al]ZSM-5. Reaction conditions: $T = 673\text{ K}$, $P = 40\text{ bar}$, and $\text{WHSV} = 375\text{--}1500\text{ g}_{\text{C}_5}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$.

conversion did not change above 30 bar, product selectivity continued to change with increasing pressure. Elevated pressures promote oligomerization of olefins,^{33–35} a reaction also observed here. Increasing pressure decreased light olefin production and increased formation of C_{6+} compounds. Although elevated pressures promote oligomerization, the larger compounds in the C_{6+} fraction eventually become more reactive and crack at

high temperatures as seen in Fig. 4. As reaction temperature increases, cracking rates of the C_{6+} fraction become greater than oligomerization rates, leading to an increase in the production of propane. Carbon selectivity of the light olefins also increased with increasing WHSV. With less time to react, a greater percentage of light olefins formed through monomolecular cracking of pentane survived without undergoing further bimolecular reactions.

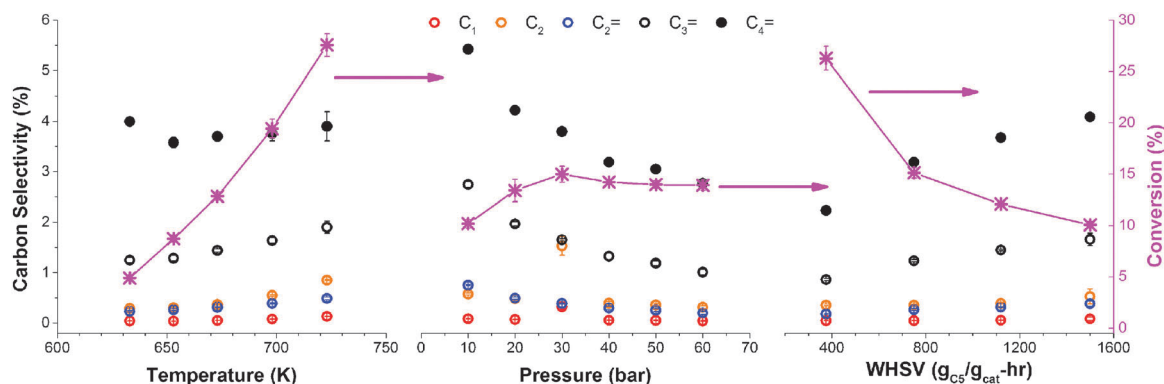


Fig. 7 Selectivity of products within the lights fraction at various temperatures (left), pressures (middle), and WHSV (right). Reaction conditions: $T = 633\text{--}723\text{ K}$, $P = 10\text{--}60\text{ bar}$, and $\text{WHSV} = 375\text{--}1500\text{ g}_{\text{C}_5}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$.

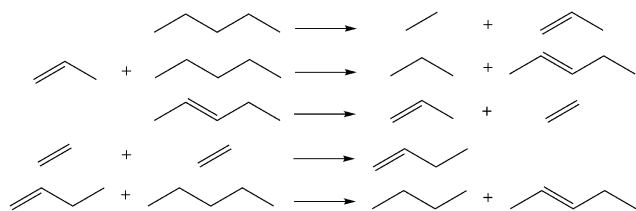


Fig. 8 Simplified reaction network demonstrating the production of propane and butane.

From the observed trends in carbon selectivity of the light olefins, a simplified reaction network can be proposed to illustrate the formation of the major products: propane and butane.

Fig. 8 displays a simplified reaction network consistent with the observed formation of propane and butane. After protolytic cracking of *n*-pentane, propene and ethane are formed and the propene then can react with another pentane *via* hydride transfer. This forms one of the major products, propane. The pentene can crack *via* beta scission to form another molecule of propene and ethene. Any ethene that is formed can dimerize to form butene. The butene can react with another pentane *via* hydride transfer yielding the second major product, butane. Through oligomerization, compounds heavier than pentane can form and subsequently crack to form lighter products or cyclize and aromatize. In reality, a more complex reaction network of monomolecular and bimolecular reactions exists, as evidenced by the product distribution and trends in activation energy.

If monomolecular cracking were the dominant reaction channel, as pressure increases, the apparent activation energy should also increase and approach the intrinsic activation energy. This trend occurs because saturation kinetics are reached at elevated pressures, reducing the effect of adsorption enthalpy on the apparent activation energy.¹¹ As seen in Fig. 9, the apparent activation energy based on consumption of *n*-pentane decreases with increasing pressure, which is opposite of the expected trend for monomolecular cracking. Furthermore, Luo *et al.* reported the intrinsic activation energy of *n*-hexane cracking on ZSM-5 to be 170 kJ mol⁻¹, while Gounder *et al.* reported the intrinsic activation energy of propane cracking on ZSM-5 to be 204 kJ mol⁻¹.^{11,15} Based on these observations, it is expected that the activation energy above the saturation pressure of *n*-pentane (> 30 bar) to be near those of propane and hexane.¹⁵ At 40 bar, the apparent activation energy for the consumption of *n*-pentane was 86 kJ mol⁻¹, which was much less than expected for monomolecular cracking, but consistent with the results obtained using other zeolite frameworks as solid acid catalysts.

Luo *et al.* recently investigated the high pressure cracking of *n*-hexane on H-USY, H-Beta, and H-Mordenite. In the work, the apparent activation energy for cracking on zeolite beta (63 kJ mol⁻¹) and USY (55 kJ mol⁻¹) did not change with pressure, while the apparent activation energy on mordenite decreased from 77 kJ mol⁻¹ at 1 bar to 66 kJ mol⁻¹ at 137 bar.¹² The activation energies observed from the cracking of hexane on USY, zeolite beta, and mordenite are consistent with those for the cracking of *n*-pentane on ZSM-5, but differ from the cracking of *n*-hexane on ZSM-5.

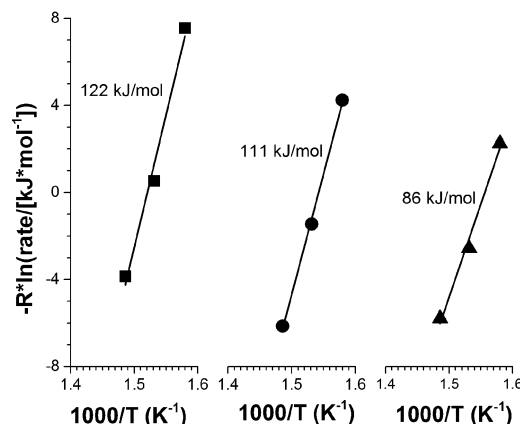


Fig. 9 Activation energies at 10 bar (square), 20 bar (circle), and 40 bar (triangle). Reaction conditions: $T = 633\text{--}673$ K, $P = 10\text{--}40$ bar, and $\text{WHSV} = 1120 \text{ g}_{\text{C}_5} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$.

Luo *et al.* also investigated the product selectivity for the cracking of *n*-hexane on ZSM-5.¹² With increasing conversion under isothermal conditions, an increase in selectivity to higher molecular weight species was observed. For the conversion of *n*-pentane on ZSM-5, increasing conversion under isothermal conditions did not result in any significant change in selectivity to higher molecular weight species. However, there were two trends in product selectivity that were similar between the conversion of pentane and hexane on ZSM-5. First, the major products of hexane conversion were butanes and pentanes, analogous to propane and butanes for pentane conversion. Second, increasing pressure caused a decrease in selectivity to light olefins for the conversion of both pentane and hexane on ZSM-5.

The decrease in activation energy with increasing pressure is evidence of a shift from a higher activation energy reaction channel to a lower activation energy reaction channel. While the conversion of pentane and hexane on ZSM-5 have similar trends in product selectivity with changing pressure, the differences in apparent activation energy suggest the conversion occurs *via* alternative reaction pathways.

5. Conclusions

The high selectivity (>70%) to propane and butane, along with the observed changes in the selectivity to lights and C_{6+} compounds, indicate that bimolecular reactions, such as hydride transfer and alkylation, control product distribution. While the product distribution from the high pressure conversion of pentane resulted in an endothermic process, hydride transfer reactions led to the transformation of high energy olefins into lower energy paraffins and aromatics, resulting in a decrease of the process endothermicity from a target of 1.1 MJ kg⁻¹ of *n*-pentane converted to an estimated 0.6 MJ kg⁻¹. Hydride transfer occurs readily on H-[Al]ZSM-5 and other zeolites, and an alternative catalyst that suppresses these reactions should improve selectivity to light olefins, which will increase cooling capacity of the endothermic fuel.

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