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Selectivity for dimers in pentene oligomerization over acid zeolites

Atish Kulkarni [a], Akshai Kumar [b], Alan S. Goldman [b], Fuat E. Celik [a,*]

[a] *Department of Chemical and Biochemical Engineering*

[b] *Department of Chemistry and Chemical Biology*

Rutgers, The State University of New Jersey, 98 Brett Road, Piscataway, NJ 08854, USA

[*] Corresponding author: Tel. +1 848 445 5558
E-mail address: fuat.celik@rutgers.edu (F.E. Celik)

Abstract

The reactions of 1-pentene over acid zeolites were investigated in the liquid phase at 473 K. The primary reactions were isomerization, dimerization, and subsequent cracking of dimers. Zeolites consisting of only 10-membered (MFI) or 12-membered rings (FAU, BEA) behaved similarly, with dimerization and subsequent cracking products observed. Zeolites possessing 8-membered ring pores (MOR, FER) showed very different selectivity from each other and from other zeolites. MOR showed almost complete conversion of C_{10} olefins, such that hexene and butene from cracking were the dominant products. FER showed high activity and selectivity for dimerization, with very small amounts of cracking products observed.

1. Introduction

Light alkanes and olefins, such as pentanes and pentenes, are formed in significant quantities during petroleum processing. For example, thermal cracking of naphtha and gas oil yields ethene (C_2) and propene (C_3) as primary products and C_5 paraffins as by-products [1–3]. Pentanes are of limited value as they are too light for direct application in liquid fuels and too heavy for use as liquefied petroleum gas. The corresponding alkenes are of greater value, and can be generated from the alkanes via catalytic dehydrogenation [4–6]. Separation of the pentanes from the pentenes is both difficult and necessary for storage [7]. Alternatively, pentene dimerization produces commercially important C_{10} olefins (decenes), which can undergo catalytic hydrogenation to form C_{10} alkanes. Decanes are suitable for use as gasoline (if highly branched) or diesel fuel (if not) blending, or even for direct use as solvents. Additionally, decenes are intermediates in the production of epoxides, amines, synthetic lubricants, alkylated aromatics, and synthetic fatty acids.

The acid-catalyzed dimerization of light olefins has been studied extensively over zeolites [8–20], mesoporous aluminosilicates [21,22], and phosphoric acid [23,24]. Brønsted acid-catalyzed reactions follow carbocation-mediated mechanisms. The relative rates of isomerization, dimerization, monomolecular and bimolecular cracking are a strong function of catalyst structure and reaction conditions (e.g. temperature, pressure, contact time). In zeolite reactions, lower temperatures tend to favor heavier products, while higher temperatures favor cracking and lighter products. Heavy products may be unable to desorb from the catalyst pores and lead to catalyst deactivation. This becomes more of a concern with heavier feed olefins, such as pentenes, as compared to lighter, more conventional feeds such as propene [15]. In high temperature (773 K) studies of cracking [25,26], zeolite frameworks with internal cavities no

larger than 0.62 nm were found to be small enough to allow monomolecular pentene cracking, while cracking on zeolites with larger pores proceeded via dimerization followed by cracking of the decenes (bimolecular cracking), primarily to hexenes and butenes. At 773 K, all of the decene that formed subsequently cracked and no C_{10} products were reported. Double bond and skeletal isomerization of pentenes have been reported over a range of temperatures from 523 K to 673 K [27,28] in gas-phase experiments over MFI, FER, and BEA zeolites, with very low yields of dimers. One study reported oligomerization of pentenes at 473 K but did not distinguish between dimers and the products of dimer and trimer cracking [15].

We report on the reactions of 1-pentene in the liquid phase at 473 K over acid-form MFI, FAU, BEA, MOR, and FER zeolites. While all zeolites showed activity for isomerization, dimerization, and subsequent cracking of dimers, FER showed high selectivity for dimers with very little cracking, in contrast to previous studies at higher temperatures which showed little selectivity for dimers [25–28]. MOR showed complete cracking of C_{10} dimers to hexene and butene, and MFI, FAU, and BEA showed intermediate activity with dimerization and cracking competing with one another.

2. Experimental

Zeolite samples were obtained commercially from Zeolyst with different Si/Al ratios in either the NH_4^+-form (MFI Si/Al = 15; FAU Si/Al = 2.6, Si/Al = 6; BEA Si/Al = 12.5; MOR Si/Al = 10; FER Si/Al = 10) or the H^+-form (FAU Si/Al = 15, Si/Al = 40). As-received samples were heated to 773 K for 3 h at the rate of 2 K min^{-1} in 100 cm^3 min^{-1} flow of dry air (zero grade) to convert from the NH_4^+ form to the H^+ form and to drive off any adsorbed water. Dried samples were stored in a desiccator prior to use to minimize subsequent adsorption of water.

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Reactions of 1-pentene were carried out in a Kontes vial in an oil bath held at a constant temperature of 473 K and stirred at 350 rpm with a magnetic stir bar. The total number of acid sites in each reaction was kept constant at 0.0119 mmoles. Because the total mmoles of acid sites were kept constant, the mass of catalyst was adjusted in each experiment. In most of the experiments reported, the mass used fell between 7.86 mg (for the Si/Al ratio =10 samples) to 11.43 mg (for the Si/Al ratio =15 samples). The ratio of masses is the same as the ratio of Si/Al ratios. For the comparison of FAU samples of differing Si/Al ratios, the range of masses used was between 2.57 and 29.29 mg, reflecting the wider range of Si/Al ratios used (between 2.6 and 40). For each reaction, 200 µL of a solution of 300 mM 1-pentene in n-dodecane was used. Reaction times include only the time the reaction vessel was submerged in the oil bath. A 0-minute reaction indicates that the reactor was not heated. Due to their low boiling points, gaseous hydrocarbon products (lighter than C_5) were not collected along with the liquid products, and were consequently not analyzed. Control experiments showed that n-dodecane did not react when pentene was present.

The atom yield and selectivity of decene were calculated on the basis of atomic carbon in measured products by the following formulae, where C_i is the measured concentration of olefin I, and t is the reaction time:

$$\% \text{ atom yield } = \frac{10 \times C_{\text{decenes at } t}}{5 \times C_{\text{pentenes at } t=0}} \times 100$$

$$\% \text{ atom selectivity } = \frac{C_{\text{decenes at } t}}{C_{\text{hexenes}} + C_{\text{heptenes}} + C_{\text{octenes}} + C_{\text{decenes}}} \times 100$$

While products lighter than C_5 were not measured directly, the above definition of atom selectivity assumes that all C_6–C_8 olefins were derived from the cracking of decene, and therefore an unquantified but equimolar quantity of C_4–C_2 was also formed. This assumption is

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an oversimplification and ignores secondary oligomerization of these lighter olefins. By assuming that all C_6–C_8 olefins were derived from the cracking of decene, this yields a lower limit for the % atom selectivity.

3. Results and Discussion

Double-bond isomerization of 1-pentene was rapid in all experiments. A distribution of 1-pentene, *cis*-2-pentene, and *trans*-2-pentene was measured even in samples before heating (i.e. 0 minutes reaction time in Figures 1 and 3), possibly reaching thermodynamic equilibrium [27]. Skeletal isomerization of reactants and products was also observed for all carbon chain lengths at all reaction times in samples heated to reaction temperature [27,28]. Therefore, all products are referred to by their carbon number and all GC peaks within the same molecular weight are reported together. Products heavier than C_{10} were not observed. Some heavier hydrocarbons (olefins, small aromatic) and/or coke (polyaromatic) species may have formed and been trapped within the zeolites, as indicated by the color change (from white to yellow/light brown) in the recovered zeolite powders [15,29].

Figure 1 shows the effect of zeolite framework type on the percent atomic yield and selectivity toward C_{10} olefins in reactions of 1-pentene over acid-form MFI, FAU, BEA, MOR, and FER. Reaction times ranged between 0 and 360 minutes, and reactions were heated at 473 K. The Si/Al ratio of all zeolites was kept in a small range between 10 and 15. This minimizes the differences in acid strength and acid site spacing as a function of Si/Al ratio. In this way, the effect of the zeolite pore size and structure could be isolated. Because the total mmoles of acid sites were kept constant in the reactions, the mass of catalyst was adjusted in each experiment. In the experiments reported, the mass used fell between 7.86 mg (for the lowest Si/Al ratio samples) to 11.43 mg (for the highest Si/Al ratio samples).

The highest percent yields of decenes, 21% over FAU and 26% over FER, were obtained at 40 minutes reaction time (Figure 1a). Of the two, FER was more selective (74%) than FAU (59%) (Figure 1 b). For both zeolites, selectivity towards decenes declined as a function of reaction time due to cracking of dimers at longer reaction times (Figure 3 b and e). MFI and BEA were very similar in C_{10} yield and selectivity, and yields for all four zeolites were comparable after 360 minutes. In contrast, MOR showed very little selectivity towards decenes at any reaction time. To compare selectivity across the different zeolite frameworks, selectivity is compared at the same conversion (~40% reached after 10 or 40 minutes of reaction time on all the samples) in Figure 2. Selectivity was not found to depend strongly on initial pentene concentration (Figure S1).
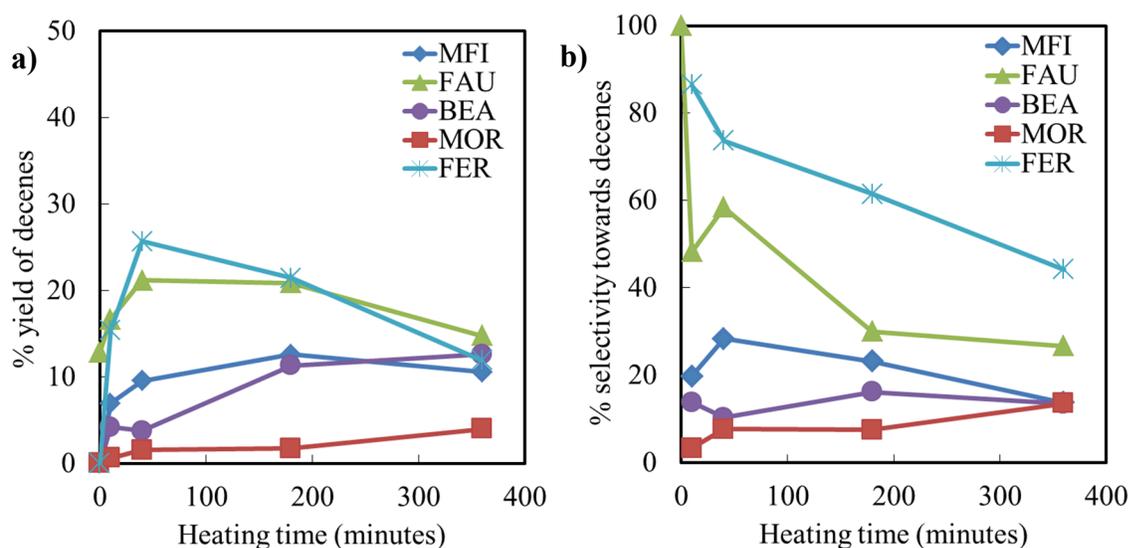

Figure 1. The effect of heating time over MFI (Si/Al = 15), FAU (Si/Al = 15), BEA (Si/Al = 12.5), MOR (Si/Al = 10), and FER (Si/Al = 10) on a) the percent yield of C_{10} olefins and b) the percent selectivity toward C_{10} olefins. 7.86 – 11.43 mg catalyst (0.0119 mmoles of acid sites). T = 473 K, $C_{pentene,initial}$ = 300 mM.
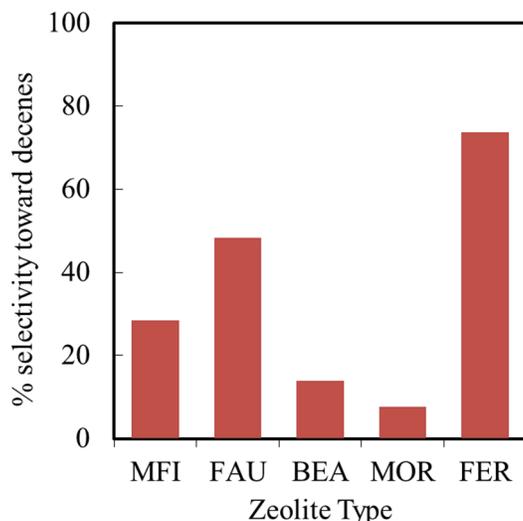
Figure 2. Percent selectivity toward decenes across zeolite types at similar conversion of 40%. 7.86 – 11.43 mg catalyst (0.0119 mmoles of acid sites). $T = 473$ K, $C_{\text{pentene, initial}} = 300$ mM.

Figure 3 shows the concentration of C_6 through C_{10} olefins for reactions at 473 K over the five zeolite samples. No C_9 olefins were observed in any reactions. This would be expected if the only species undergoing cracking are C_{10} olefins, due to the high activation energy for the formation of C_1 products from such pathways [25,26,30–33]. The absence of C_9 products indicates that trimers did not form during these reactions. The trimerization of pentenes would produce C_{15}, and the subsequent cracking of C_{15} would form C_9 olefins, (whether or not the trimers desorbed from the catalyst). Since the lack of C_9 formation excludes the formation of trimers, the cracking products C_6, C_7, and C_8 were derived primarily from the cracking of dimers (C_{10}) into C_6 and C_4, C_7 and C_3, and C_8 and C_2. The gaseous C_2-C_4 cracking products were not quantified in these experiments.

The distribution of C_6-C_8 cracking products were similar over MFI, FAU, and BEA (Figures 3a-c), with the concentrations of $C_6 > C_7 > C_8$. This is consistent with the order of stability for the complementary isobutyl, propyl, and ethyl carbocation intermediates formed during decene cracking. The C_6/C_7 ratios were nearly constant and equal amongst these three

zeolites for all reaction times. On MFI and BEA, the C_6/C_8 ratio at different reaction times remained nearly constant. However, over FAU the C_8 concentration grew much less than either the C_6 or C_7 concentrations for reaction times longer than 40 minutes. C_8 cracking may be enhanced in the larger pores of FAU, which better accommodate the larger transition state for the cracking of octyl carbocations. This would lead to a lower concentration of C_8 olefins in reactions over FAU. MFI and BEA both possess smaller internal cavities than FAU [34] which may suppress C_8 cracking [20]. The coupling of lighter C_2–C_4 cracking products may be increasing the concentration of the observed products and causing small variations in the ratios of these products at different reaction times.

Reaction temperatures above 473 K led to very low selectivity to dimers, consistent with previous investigations [25–28]. Significant coke deposits also formed at these higher temperatures, and zeolite powders turned black after reaction. FAU was unique amongst zeolites tested in that it showed activity at room temperature (0 minutes of heating in Figure 3b). Nearly 20 mM decenes formed during the time required to prepare the reaction, roughly 10 minutes, at room temperature. No other products were observed at 10 minutes. This decene yield is at least as large as that seen on MFI and BEA after 180 minutes of heating at 473 K, and larger than any yield achieved over MOR. No other products were observed at 10 minutes. At 40 minutes, decene yield increased slightly and cracking products were observed. While selectivity for dimerization was highest at low temperatures, it may be desirable to incorporate dimerization into processes that require higher temperature.

MOR showed very different product distributions from the other zeolites (Figure 3d-e). MOR possessed very high selectivity for cracking dimers to C_6 (and C_4, not measured), with almost no C_{10} olefins in the products, and very little C_7 and C_8. The concentration of the primary

observed product hexenes was almost constant as a function of reaction time after 40 minutes, indicating nearly complete deactivation of the catalyst. While 10-membered ring (MFI) and 12-membered ring zeolites (FAU and BEA) formed multiple cracking products, MOR, which possesses both 12-membered rings as well as 8-membered ring side pockets, showed a unique ability to disproportionate pentene to hexene and butene. The smaller side pockets of MOR, which are very different from the 8-membered rings of FER, are known to have unique reactivity [35], and are possibly too small to accommodate the formation of heptenes and octenes, leading to the high preference for hexenes. Given the commercial importance of hexenes and butenes relative to pentenes, MOR may have value in selective conversion of pentenes to C_4 and C_6 olefins.

FER showed very high C_{10} selectivity from 1-pentene, with very low cracking activity compared to the other zeolites tested, especially at shorter reaction times (Figure 3 e). Recent results for 1-butene oligomerization over FER at low temperatures (373 to 523 K) were also found to proceed with high selectivity to dimers (C_8) [20]. The low bimolecular cracking rate over FER can be explained by the confinement experienced by the decenes in the smaller pores of FER [20,26]. At longer reaction times, the concentration of C_{10} olefins declined and more cracking products could be seen. Unique to FER, the concentration of C_7 olefins was less than that of C_8 olefins. Together with literature reports, FER appears to be highly selective for temperature-dependent 1-pentene conversion; dimerization at 473 K (this work), isomerization at 673 K [28], and monomolecular cracking at 773 K [26]. The same spatial confinement that prevents cracking of C_{10} species via a bimolecular mechanism promotes monomolecular cracking at 773 K and decene desorption at 473 K.

The effect of zeolite acid site proximity was investigated by varying the Si/Al ratio of FAU while holding the total concentration of acid sites constant (Figure S2). As was reported with propene dimerization over MFI [18], the optimum selectivity was obtained at a low Si/Al ratio (6 for FAU, 12 for MFI). Further decreasing the Si/Al ratio did not improve the selectivity as acid site strength variations became significant at Si/Al = 2.6.

4. Conclusions

The effect of zeolite framework type on reactions of 1-pentene at 473 K in the liquid phase was investigated using commercially available MFI, FAU, BEA, MOR, and FER zeolites. All zeolites catalyzed rapid double bond isomerization, even at room temperature, and skeletal isomerization upon heating to reaction temperature. FER showed high selectivity for dimerization, with very little bimolecular cracking activity and the highest decene yield. Pentene conversion over FER switches from selective dimerization at lower temperature (473 K) to selective monomolecular cracking at high temperature (773 K). MOR showed a unique selectivity for disproportionation of pentenes to more commercially important hexenes and butenes. These unique selectivities can be explained by molecular confinement in the narrow pores of FER and the 8-membered ring side pockets of MOR respectively.
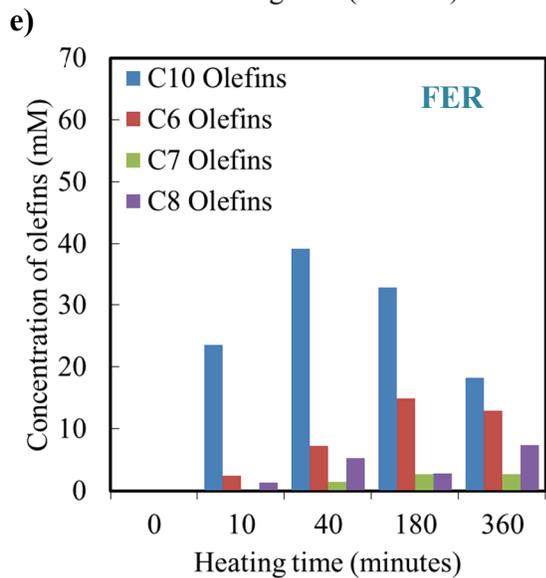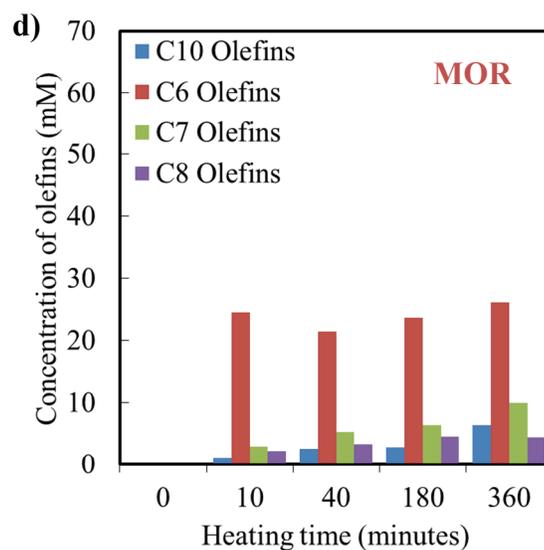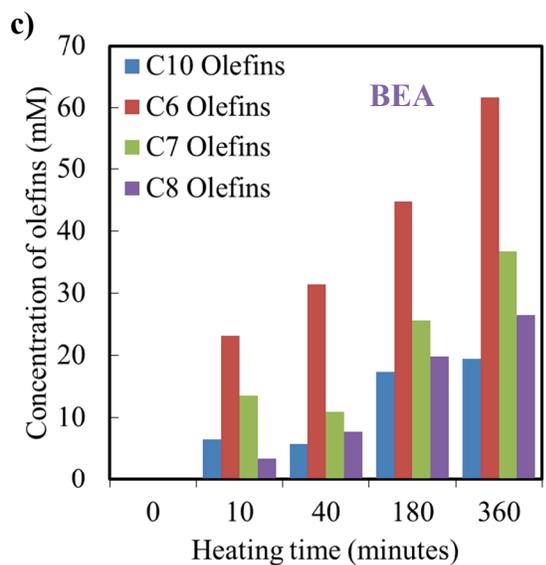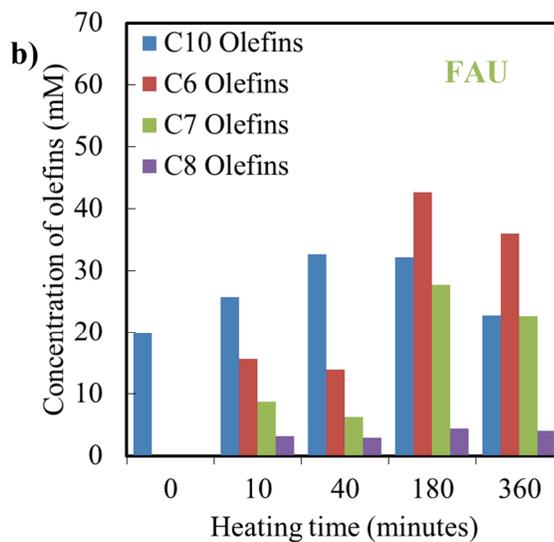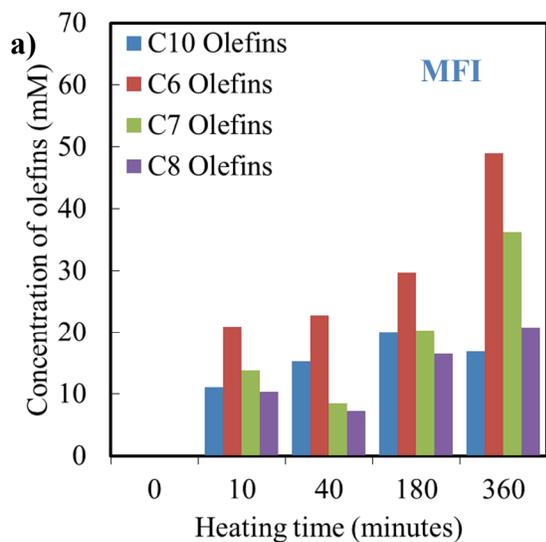
Figure 3. The concentration of olefins ($C_6 - C_{10}$) observed as function of heating time over a) MFI (Si/Al = 15), b) FAU (Si/Al = 15), c) BEA (Si/Al = 12.5), d) MOR (Si/Al = 10), and e) FER (Si/Al = 10). 7.86 – 11.43 mg catalyst (0.0119 mmoles of acid sites). T = 473 K, $C_{pentene,initial}$ = 300 mM.

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Supplementary Information

The effect of initial pentene concentration on dimerization selectivity is shown for one representative reaction over FAU (Si/Al = 6) in Figure S1. The selectivity was not found to depend strongly on initial pentene concentration.
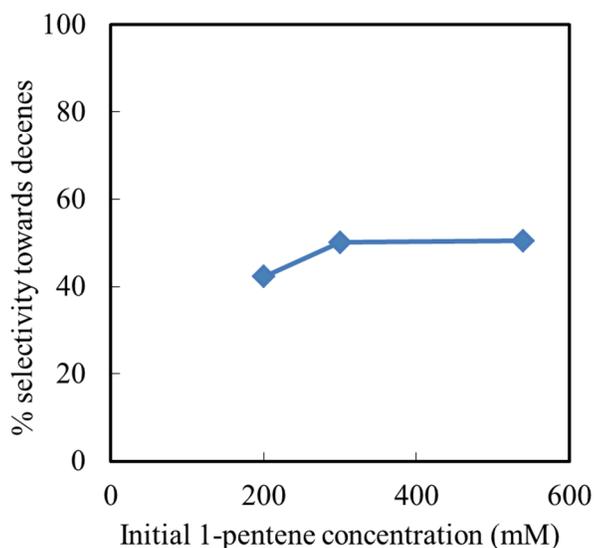

Figure S1. The effect initial 1-pentene concentration over FAU (Si/Al = 6) on the percent selectivity toward C_{10} olefins produced by C_5 dimerization. 5 mg catalyst (0.0119 mmoles of acid sites). $T = 473$ K.

The effect of zeolite acid site proximity was investigated by varying the Si/Al ratio of FAU while holding the total concentration of acid sites constant (Figure S2). As was reported with propene dimerization over MFI [18], the optimum selectivity was obtained at a low Si/Al ratio (6 in this study, 12 for MFI). Further decreasing the Si/Al ratio did not improve the selectivity as acid site strength variations become significant at Si/Al = 2.6. FAU samples with Si/Al ratios of 2.6, 6, 15 and 40 were used. Figure S2 shows the effect of Si/Al ratio on the percent yield and selectivity of C_{10} olefins by oligomerization of C_5 olefins as a function of heating time at 473 K. The highest yield was achieved over Si/Al = 6, where the concentration of decenes increased quickly up to 40 minutes, and then remained nearly constant up to 360 minutes. This led to a near-constant selectivity of roughly 50%, as opposed to a declining selectivity over Si/Al ratio of 15.
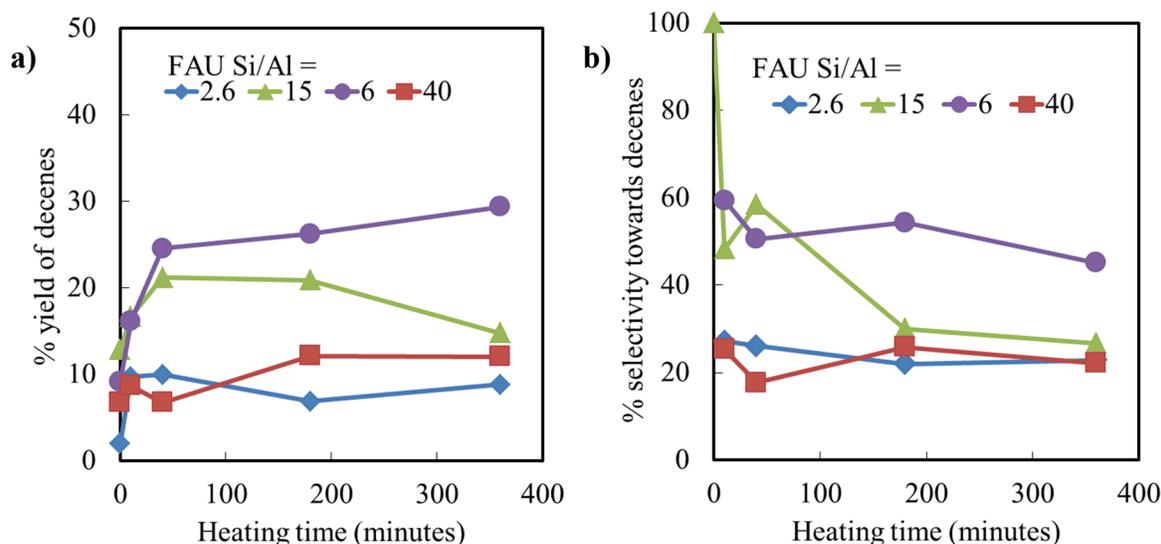
Figure S2. The effect of heating time over FAU (Si/Al = 2.6, 6, 15 and 40) on a) the percent yield of C_{10} olefins and b) the percent selectivity toward C_{10} olefins produced by C_5 dimerization. 2.57 – 29.29 mg catalyst (0.0119 mmoles of acid sites). T = 473 K, $C_{pentene, initial}$ = 300 mM.

A summary of the properties of all zeolites used in this study are provided in Table S1.

Table S1. Summary of Zeolite Parameters

Zeolite Type	Zeolyst[a] product code	Si/Al ratio [b]	Pore Ring [c]	Pore Dimensions	Pore entrance diameter (Å) [1]	Maximum Sphere Diameter (Å) [d] [2]	
						Included	Diffusing
MFI (ZSM-5)	CBV 3024E	15	10 MR 10 MR	3	5.6 × 5.3 5.5 × 5.1	6.36	4.46
FAU (faujasite)	CBV 500	2.6	12 MR	3	7.4	11.18	7.29
	CBV 712	6					
	CBV 720	15					
	CBV 780	40					
BEA* (beta)	CP814E*	12.5	12 MR 12 MR	3	6.7 × 6.6 5.6 × 5.6	6.62	6.07
MOR (mordenite)	CBV 21A	10	12 MR 8 MR	1	7.0 × 6.5 5.7 × 2.6	6.64	6.39
FER (ferrierite)	CP914C	10	10 MR 8 MR	2	5.4 × 4.2 4.8 × 3.5	6.25	4.63

[a] Zeolite samples were obtained commercially from Zeolyst.
 with different Si/Al ratios in either the NH4+-form (MFI Si/Al = 15; FAU Si/Al = 2.6, Si/Al = 6; BEA Si/Al = 12.5; MOR Si/Al = 10; FER Si/Al = 10) or the H+-form (FAU Si/Al = 15, Si/Al = 40).
[b] Nominal Si/Al ratio reported by Zeolyst
[c] Number of Al and Si T-atoms in pore opening ring in major channel system(s). MR = membered-ring

[d] Maximum size of a hard sphere that can be included in or diffuse freely through the zeolite pores

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