

## Short communication

## Selectivity for dimers in pentene oligomerization over acid zeolites



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## 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 rings (MOR, FER) showed very different selectivity from each other and from other zeolites. MOR showed almost complete conversion of C<sub>10</sub> 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.

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## 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<sub>2</sub>) and propene (C<sub>3</sub>) as primary products and C<sub>5</sub> paraffins as by-products [1–23]. 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<sub>10</sub> olefins (decenes), which can undergo catalytic hydrogenation to form C<sub>10</sub> 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, and 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<sub>10</sub> 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<sub>10</sub> 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<sub>4</sub><sup>+</sup>-form (MFI Si/Al = 15; FAU Si/

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Al = 2.6, Si/Al = 6; BEA Si/Al = 12.5; MOR Si/Al = 10; FER Si/Al = 10) or the H<sup>+</sup>-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<sup>-1</sup> in 100 cm<sup>3</sup> min<sup>-1</sup> flow of dry air (zero grade) to convert from the NH<sub>4</sub><sup>+</sup> form to the H<sup>+</sup> form and to drive off any adsorbed water. Dried samples were stored in a desiccator prior to use to minimize subsequent adsorption of water.

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-min reaction indicates that the reactor was not heated. Due to their low boiling points, gaseous hydrocarbon products (lighter than C<sub>5</sub>) 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<sub>i</sub> 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<sub>5</sub> were not measured directly, the above definition of atom selectivity assumes that all C<sub>6</sub>–C<sub>8</sub> olefins were derived from the cracking of decene, and therefore an unquantified but equimolar quantity of C<sub>4</sub>–C<sub>2</sub> was also formed. This assumption is an oversimplification and ignores secondary oligomerization of these lighter olefins. By assuming that all C<sub>6</sub>–C<sub>8</sub> olefins were derived from the cracking of decene, this yields a lower limit for the % atom selectivity.

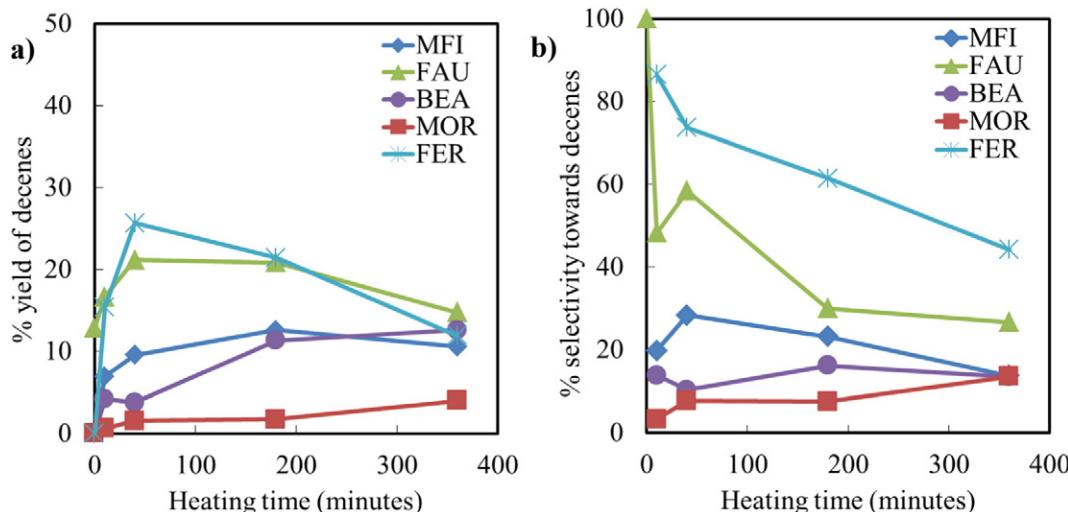


Fig. 1. The effect of heating time over MFI (Si/Al = 15), FAU (Si/Al = 15), BEA (Si/Al = 12.5), MOR (Si/Al = 10), and FER (Si/Al = 10) on a) the percent yield of C<sub>10</sub> olefins and b) the percent selectivity toward C<sub>10</sub> olefins. 7.86–11.43 mg catalyst (0.0119 mmoles of acid sites). T = 473 K, C<sub>pentene,initial</sub> = 300 mM.

### 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 min reaction time in Figs. 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<sub>10</sub> were not observed. Some heavier hydrocarbons (olefins, small aromatic) and/or coke (polycyclic aromatic) 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].

Fig. 1 shows the effect of zeolite framework type on the percent atomic yield and selectivity toward C<sub>10</sub> olefins in reactions of 1-pentene over acid-form MFI, FAU, BEA, MOR, and FER. Reaction times ranged between 0 and 360 min, 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 min reaction time (Fig. 1a). Of the two, FER was more selective (74%) than FAU (59%) (Fig. 1 b). For both zeolites, selectivity toward decenes declined as a function of reaction time due to cracking of dimers at longer reaction times (Fig. 3 b and e). MFI and BEA were very similar in C<sub>10</sub> yield and selectivity, and yields for all four zeolites were comparable after 360 min. In contrast, MOR showed very little selectivity toward 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 min of reaction time on all the samples) in Fig. 2. Selectivity was not found to depend strongly on initial pentene concentration (Figure S1).

Fig. 3 shows the concentration of C<sub>6</sub> through C<sub>10</sub> olefins for reactions at 473 K over the five zeolite samples. No C<sub>9</sub> olefins were observed in any reactions. This would be expected if the only species undergoing cracking are C<sub>10</sub> olefins, due to the high activation energy for the formation of C<sub>1</sub> products from such pathways [25,26,30–33]. The absence of

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