# 1-Hexene Oligomerization in Liquid, Vapor, and Supercritical Phases over Beidellite and Ultrastable Y Zeolite Catalysts

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**1-Hexene was oligomerized at 200°C and a pressure of 5 MPa in a down-flow fixed-bed tubular reactor filled with beidellite or ultrastable Y zeolite catalysts. Vapor, liquid, and supercritical states of the reacting hydrocarbons in the reactor tube were established by using propane, pentane, octane, and dodecane as solvents. The initial activity, stability with operation time, and selectivity are very dependent on the physical state of the hydrocarbons. Highest activity and stability are reached in the liquid phase using octane and dodecane solvent. The chain length of the solvent has a strong influence on the deactivation of the catalyst, on the oligomerization selectivity and on the formation of $C_6$ saturates and cracked products.** © 1998 Academic Press

*Key Words:* **1-Hexene oligomerization; hydrogen transfer reactions; ultrastable Y zeolite; beidellite; solvent effect.**

## 1. INTRODUCTION

Acid catalyzed oligomerization of $C_3^=$-$C_4^=$ alkenes produced by FCC (fluid catalytic cracking) into high-quality gasoline-range iso-olefins ($C_6^=$-$C_{10}^=$) are established petrochemical processes (1–3). The oldest process using silica supported phosphoric acid dates back to 1935 (1). Medium-pore, shape-selective acid zeolites such as H-ZSM-5 have superior activities and durabilities in the processes designated as "MOGD" (Mobil olefins to gasoline and distillate) (4–8). Large-pore zeolites with high silica-to-alumina ratio (9–11) and cation-exchanged clays (12) can be used to oligomerize terminal and internal long-chain $C_{10}^=$-$C_{20}^=$ *n*-alkenes into synthetic lubricant base stocks. In contrast to the short and long *n*-alkenes, literature data on the oligomerization of alkenes with carbon numbers in the range $C_5^=$-$C_7^=$ is more scarce. In patents dealing with alkene oligomerization, processes and catalysts are often claimed to be suitable for $C_2$-$C_{12}$ feedstocks, but in these patents, examples on $C_5^=$-$C_7^=$ alkenes are seldomly provided. Garwood reported the conversion of $C_2$-$C_{10}$ alkenes on H-ZSM-5 zeolite in a vapor phase process at temperature of 200–260°C.

Under such reaction conditions, the alkene undergoes oligomerization, isomerization, cracking to a mixture of intermediate olefins that is independent of the nature of the feedstock, and copolymerization to give a product containing all carbon numbers (13). Tabak claimed the used of H-ZSM-12 zeolite catalysts in a liquid phase process at low temperatures. In these processes, 1-hexene and 1-octene underwent selective dimerization reactions (14).

Kerosene consumption and, especially in Europe, diesel consumption are increasing. One possibility to produce these fractions is through oligomerization of $C_5^=$-$C_7^=$ FCC alkenes via acid catalysis. In this paper, we have studied the oligomerization of 1-hexene as a model compound representative of this fraction over two solid acid catalysts, acid beidellite, and ultrastable Y zeolite. We compared gas, liquid, and supercritical reaction conditions in a search for catalyst operation conditions giving high conversion, slow deactivation, and high oligomerization selectivity.

## 2. EXPERIMENTAL

Beidellite was synthesized according to a procedure reported by Le Dred and Baron (15). The as-synthesized beidellite sample was $NH_4$-exchanged and freeze-dried to obtain a powder with B.E.T. specific surface area of 62 $m^2 \cdot g^{-1}$. The sample does not contain any microporosity, has a mesopore volume of 0.159 $cm^3 \cdot g^{-1}$ as derived from $N_2$ physisorption isotherms at 77 K, and a Si/Al atomic ratio in the tetrahedral layer, assuming absence of Al-O-Al linkages, was 4.7 (15). The ultrastable Y zeolite powder sample with Si/Al atomic ratio of ca 15 was from PQ (code name CBV-720). Compared to beidellite, the US-Y zeolite presents a higher B.E.T. specific surface area (658 $m^2 \cdot g^{-1}$), with micropore and mesopore volumes of 0.253 $cm^3 \cdot g^{-1}$ and 0.122 $cm^3 \cdot g^{-1}$, respectively. This ultrastable Y zeolite and pillared versions of beidellite present a similar acidity and catalytic activity in hydroisomerization–hydrocracking of decane (16–17).

Catalyst powders were compressed into wafers that were crushed and sieved to obtain particles with diameters of 250–500 $\mu$m for use in the catalytic experiments. The

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## TABLE 1

### Reaction Conditions

| Exp. run | Catalyst | Flow-rate $(g_{olefin} \cdot g_{cata}^{-1} \cdot h^{-1})$ | Solvent (wt% in feed) | T (°C) | P (MPa) | Physical state |
|---|---|---|---|---|---|---|
| A | Beidellite | 3 | Propane (70%) | 200 | 5 | Vapor |
| B | Beidellite | 3 | Pentane (70%) | 200 | 5 | Supercritical |
| C | Beidellite | 3 | Octane (70%) | 200 | 5 | Liquid |
| D | Beidellite | 3 | Dodecane (70%) | 200 | 5 | Liquid |
| E | US-Y | 1 | Pentane (90%) | 200 | 1 | Vapor |
| F | US-Y | 1 | Pentane (90%) | 200 | 5 | Supercritical |
| G | US-Y | 3 | Octane (70%) | 200 | 5 | Liquid |
| H | US-Y | 3 | Dodecane (70%) | 200 | 5 | Liquid |

catalyst pellets were activated *in situ* in the reactor tube by a calcination under flowing oxygen ($3 \text{ cm}^3 \cdot \text{s}^{-1} \cdot \text{g}^{-1}$) during 5 h at 450°C.

1-Hexene (97%), hexane (>99%), heptane (>99%), octane (>99%), and dodecane (>99%) were from Acros, propane (>99.9%) from Alphagaz, and pentane (>99%) from Lab-Scan Analytical Science.

The 1-hexene conversions were carried out in a down-flow fixed-bed tubular microreactor. The stainless steel tube holding 0.5–3 g of catalyst between two plugs of quartz wool had an internal diameter of 1 cm and a length of 10 cm and was mounted in a tubular furnace. The dead volume inside the reactor tube was filled with glass beads with a same diameter as the catalyst particles. The temperature in the catalyst bed was monitored with an axially mounted thermocouple. The feedstock mixtures were prepared by mixing pure compounds in a pressure vessel equipped with stirrer. Heptane was used as internal standard. The feed was delivered to the reactor through a mass flow controller for liquids (Rosemount/Brooks Instruments B.V., type 5881), and the pressure in the reactor regulated with a back-pressure regulator. The reactor was pressurized with nitrogen before feeding the hydrocarbons.

The reaction products were sampled at high pressure using a sampling valve with an internal volume of 0.1 $\mu$l, located upstream of the back-pressure regulator, and transferred by means of a heated transfer line to a gaschromatograph (HP 5890 Series II) equipped with a fused silica WCOT column (CP-SiL 5 CB from Chrompack; length of 50 m, internal diameter of 0.32 mm; film thickness of 5,0 $\mu$m) and F.I.D. detector.

Liquid product fractions were collected in a gas–liquid separator at 15°C and atmospheric pressure. The skeletal branching of the oligomers was analyzed using a catalytic hydrogenation module (modified TCT injection system from Chrompack using Pd catalyst at 180°C), mounted at the inlet side of the same type of gaschromatograph as for the on-line analysis. Identification of the products was done using reference samples obtained by hydroisomerization of dodecane and using GC/MS.

## 3. RESULTS AND DISCUSSION

### 3.1. Beidellite Catalyst

The oligomerization of 1-hexene was performed on the beidellite catalyst at a temperature of 200°C, a pressure of 5 MPa, and either propane, pentane, octane, or dodecane as solvent, representing 70 wt% of the mixture (Table 1). The physical state of the hydrocarbon mixtures under reaction conditions can be estimated from the phase diagrams of the *n*-alkane solvents and considering a partial pressure of 3.5 MPa (Fig. 1). With propane, the vapor phase is established in the reactor; with pentane, the supercritical state. With octane and dodecane, the reactor is operating under liquid phase conditions. The reaction products obtained were divided into four groups: 1-hexene isomers, oligomers, cracked products, and $C_6$-hydrogenated products. The following isomers of 1-hexene were formed: *t*-2-hexene, *c*-2-hexene, 2-methyl-2-pentene, 3-methyl-*t*-2-pentene, and 3-methyl-*c*-2-pentene. In view of the purpose of our study, all $C_6^=$ products were lumped and considered as unconverted "hexene." The $C_6$ hydrogenated products formed were hexane, 2-methylpentane, and 3-methylpentane. The oligomers formed were dimers ($C_{12}^=$) essentially, together with trace quantities of trimers ($C_{18}^=$). Owing to the large quantities of $C_{12}$ formed, it was not possible to separate and analyze the small amount of $C_9^=$-$C_{11}^=$ products accurately. Therefore, the $C_{9+}^=$ fraction has been lumped and considered as oligomers, realizing that $C_9^=$-$C_{11}^=$ belong strictly speaking to the cracked product fraction. The remaining products have carbon numbers of $C_3$-$C_5$, $C_7$, and $C_8$ and are regarded as cracked products. The $C_4$ and especially the $C_5$ fraction contained significant amounts of alkanes next to alkenes.

The evolution with time-on-stream of the hexene conversion over the beidellite catalyst is shown in Fig. 2. The initial hexene conversion decreases in the solvent order:
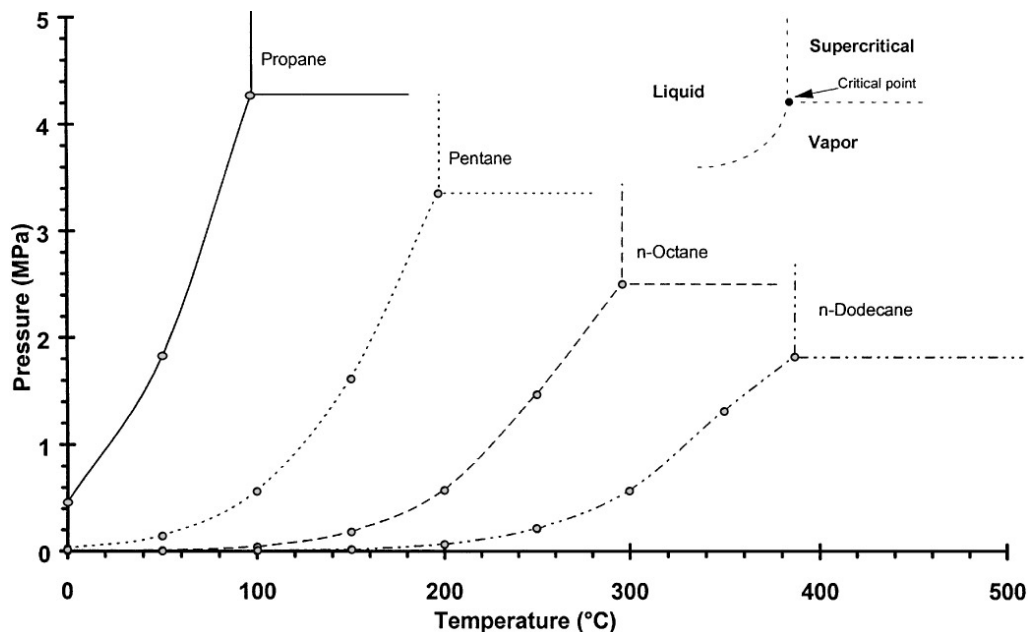
$$\text{dodecane (89\%)} \sim \text{octane (86\%)} > \text{pentane (74\%)}$$
$$> \text{propane (30\%).} \qquad [1]$$
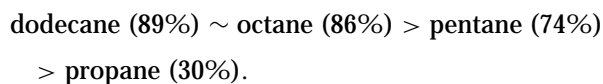
**FIG. 1.** Physical state of alkanes depending on pressure and temperature.

In the vapor phase, a low and stable conversion of ca 30% is obtained in the first 16 h. Possibly, the catalyst underwent a fast deactivation in the first hour of the experiment. The black color of the catalyst after the test was indicative of severe coking. In the supercritical phase and in presence of pentane, the catalyst was initially more active but a rapid deactivation took place in the first 16 h. In the experiments in the liquid phase, in presence of octane or dodecane solvents, the initial conversion as well as the stability of the catalyst were considerably better. In about 16 h on-stream, the hexene conversion decreased from ca 90% to 60% in the presence of octane, and from ca 90% to 70% in presence of dodecane, indicating that the stability of the catalyst is improved when using a heavier alkane solvent. Catalysts operated under the liquid phase conditions had a yellow color after the testing, suggesting less coke deposition.

The selectivities obtained under the different operation conditions of the beidellite catalyst at three conversion
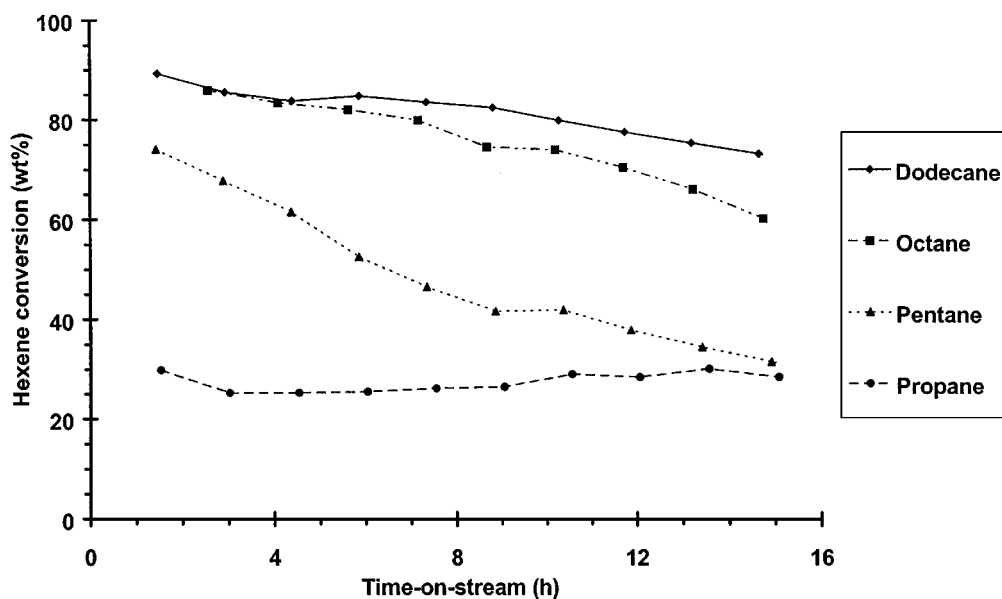


**FIG. 2.** Evolution with time-on-stream of the hexene conversion in propane, pentane, octane, and dodecane over beidellite catalyst: ◆, dodecane; ■, octane; ★, pentane; ●, propane.

**TABLE 2**

**Selectivity of Hexene Conversion and Dimer Skeletal Distribution Obtained on Beidellite Catalyst**

| Run | A | | B | | C | | D | |
|---|---|---|---|---|---|---|---|---|
| Solvent | Propane | | Pentane | | Octane | | Dodecane | |
| Physical state | Vapor | | Supercritical | | Liquid | | Liquid | |
| Time-on-stream (h) | 1.5 | 15 | 1.5 | 15 | 1.5 | 9 | 1.5 | 13.5 |
| Hexene conversion (wt%) | 30 | 34 | 74 | 33 | 86 | 74 | 86 | 76 |
| Cracking | | | | | 6 | | 8 | |
| $C_6$ saturates formation | | | | | 18 | | 26 | |
| Oligomerization | | | | | 76 | | 66 | |
| Cracking | | | 4 | | | 3 | | 6 |
| $C_6$ saturates formation | | | 34 | | | 19 | | 22 |
| Oligomerization | | | 62 | | | 78 | | 72 |
| Cracking | 3 | 3 | | 1 | | | | |
| $C_6$ saturates formation | 75 | 76 | | 71 | | | | |
| Oligomerization | 22 | 21 | | 28 | | | | |
| Skeletal dimer distribution (wt%) | | | | | | | | |
| Monobranched + Normal | 7 | | 7 | | 18 | | 24 | |
| Dibranched | 83 | | 89 | | 79 | | 70 | |
| Tribranched | 10 | | 4 | | 3 | | 6 | |
| Monobranched dimer distribution (wt%) | | | | | | | | |
| 5-Ethyldecane | 8.6 | | | | 6.7 | | | |
| 5-Methylundecane | 58.0 | | | | 59.9 | | | |
| 4-Ethyldecane | 17.3 | | | | 18.9 | | | |
| 2 & 4 Methylundecane + 3 Ethyldecane | 7.8 | | | | 6.4 | | | |
| 3-Methylundecane | 6.7 | | | | 6.2 | | | |
| n-Dodecane | 1.7 | | | | 1.8 | | | |

levels reached after specific times-on-stream in the experiments of Fig. 1 (ca 85%, 75%, and 30%) are given in Table 2. In the liquid phase with octane and dodecane solvent, the selectivities did not change substantially with the time span of the experiment and upon deactivation (Table 2). Comparing the solvents at a same conversion level obtained after different degrees of deactivation, the selectivity for oligomerization decreases in the solvent order (Table 2):

$$\text{octane} > \text{dodecane} > \text{pentane} > \text{propane.} \qquad [2]$$

The selectivity for $C_6$ saturates formation increases in the opposite order, while the cracking is little influenced (Table 2).

The $C_{12}$ fraction is mainly composed of dibranched isomers, together with monobranched isomers and small amounts of tribranched isomers (Table 2). The monobranched $C_{12}$ fraction, collected in the experiments with propane and octane, was analyzed in detail using the GC with sample hydrogenation facility (Table 2). The main products in this fraction are 5-methylundecane and 4-ethyldecane. These skeletal structures are primary products resulting from the addition of 1-hexene to hex-2-yl and hex-3-yl cations, respectively (Scheme 1). Isomers with other
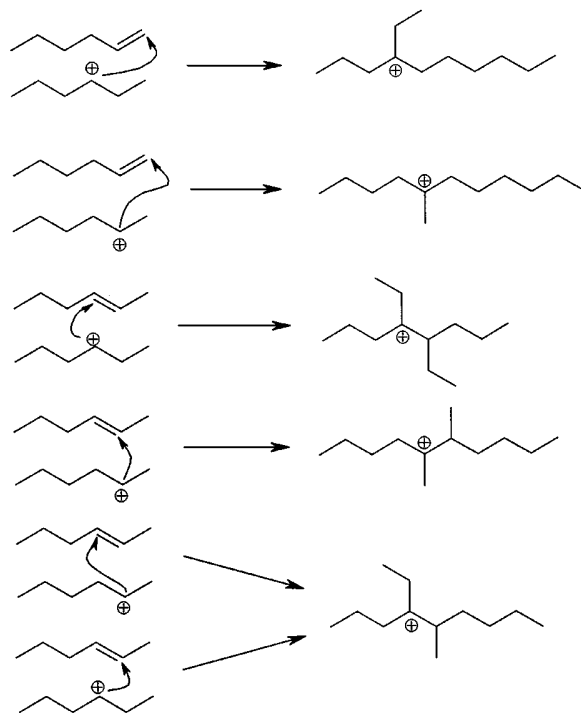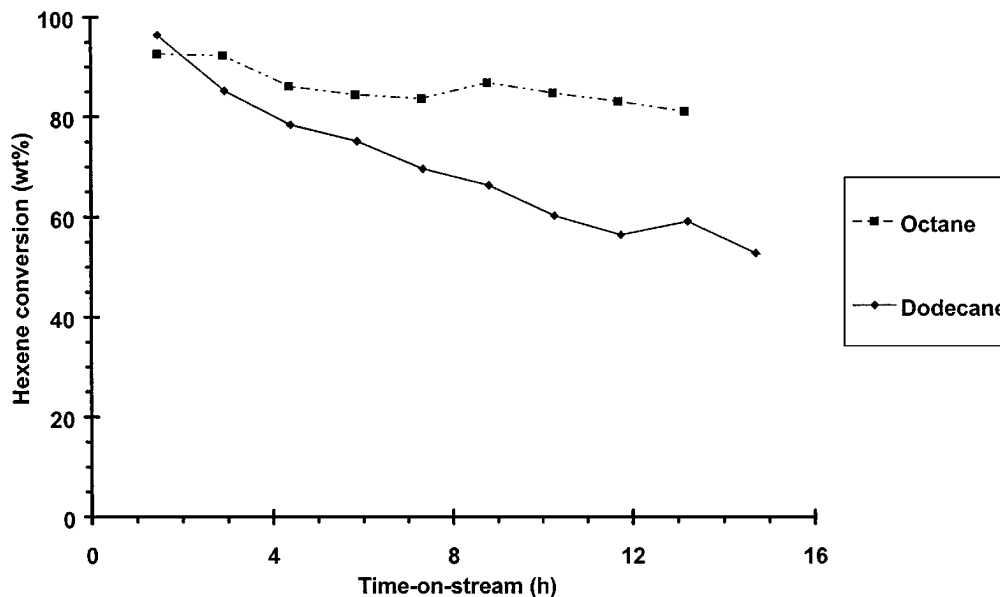


**SCHEME 1**

**FIG. 3.** Evolution with time-on-stream of the hexene conversion in octane and dodecane over ultrastable Y zeolite: ■, octane; ◆, dodecane.

branching positions are formed in small quantities indicating that alkyl shifts are relatively slow under these conditions. The small quantity of *n*-dodecane formed by unbranching of monobranched isomers is another indication that secondary isomerization is insignificant. The occurrence of secondary isomerization does not seem to be much dependent on the reaction conditions (Table 2). The composition of the monobranched $C_{12}$ products obtained in propane solvent in the vapor phase and at 30 to 34% conversion is very similar to that obtained in octane solvent in the liquid phase and at 86 to 74% conversion.

In the dibranched fraction, two main products could be identified, viz. 5,6-dimethyldecane and 4-ethyl,5-methylnonane. These are expected primary dimerization products (Scheme 1). Quantification of the dibranched $C_{12}$ composition was, however, not possible given the severe overlapping of GC peaks.

It can be concluded that the reaction conditions have a strong impact on saturates formation and deactivation, but much less on the oligomerization mechanism and secondary isomerization of the hexene dimers.

### 3.2. Ultrastable Y Zeolite Catalysts

The ultrastable Y zeolite catalyst was used in a variety of reaction conditions in order to verify whether the observations made with beidellite can be generalized (Table 1). In the experiments in octane and dodecane at 200°C and a pressure of 5 MPa, high hexene conversions exceeding 90% were reached initially (Fig. 3 and Table 3). In supercritical pentane at the same pressure and temperature, the hexene conversion reaches initially 75% only, even at three times lower space velocity (Table 3). Using pentane and a pres-

sure of 1 MPa leads to vapor phase conditions (Fig. 1) and a low initial hexene conversion (45%, Table 3). As with beidellite, the activity of the ultrastable Y zeolite decreases in the following order of physical states for the hydrocarbons:

$$\text{liquid phase} > \text{supercritical phase} > \text{vapor phase.} \quad [3]$$

Competitive physisorption phenomena between reagent, product, and solvent molecules could be at the origin of this influence of the physical state. Propane and pentane molecules with a lower molecular weight than the hexene dimers are less effective for evacuation of the oligomerization products from the catalyst and cause fast deactivation.

On ultrastable Y, the highest oligomerization selectivity was obtained in octane (62% at 93% conversion, Table 3). In dodecane and at a similar conversion, it was 52% only (Table 3). This difference is due to a higher selectivity for $C_6$ saturates (21% in dodecane, compared to 13% in octane, Table 3), while the cracking selectivity is little influenced.

**TABLE 3**

**Selectivity of Hexene Conversion on Ultrastable Y Zeolite**

| Run | E | F | G | H |
|---|---|---|---|---|
| Solvent | Pentane | Pentane | Octane | Dodecane |
| Physical state | Vapor | Supercritical | Liquid | Liquid |
| Time-on-stream (h) | 1.5 | 1.5 | 1.5 | 1.5 |
| Hexene conversion (wt%) | 45 | 75 | 93 | 96 |
| Cracking | 12 | 14 | 23 | 27 |
| $C_6$ saturates formation | 62 | 40 | 13 | 21 |
| Oligomerization | 26 | 46 | 62 | 52 |

There is one main difference between the behavior of the zeolite and the clay. The ultrastable Y zeolite deactivates faster in dodecane than in octane (Fig. 3), while the opposite is observed for beidellite (Fig. 2). The zeolite contains micropores and mesopores, while the clay material is essentially meso and macroporous. On beidellite, as well as ultrastable Y, hydrogen transfer reactions to produce saturates are more important in dodecane than in octane (Tables 2 and 3). It can be speculated that in the zeolite, the hydrogen deficient molecules cause deactivation by micropore blockage, whereas in the clay with its larger pores they are more easily desorbed. It remains to be explained why the hydrogen transfer reactions are less important in octane, compared to dodecane, and this is independent of the nature of the catalyst.

## 4. CONCLUSIONS

The activity, stability, and selectivity of beidellite and ultrastable Y zeolite in 1-hexene oligomerization are strongly influenced by the physical state of the hydrocarbons under reaction conditions. With both catalysts, liquid phase reaction conditions achieved by using octane and dodecane solvents are most appropriate with respect to catalytic activity, oligomerization selectivity, and stability. Under liquid phase conditions, the molecular weight of the solvent has a strong influence on the selectivity and the stability of the catalyst. On beidellite as well as on ultrastable zeolite Y, hydrogen transfer reactions resulting in the formation of $C_6$ saturates are the main side reactions. These hydrogen transfer reactions are more abundant in dodecane than in octane. Deactivation seems to be linked to the formation of large hydrogen deficient molecules, blocking micro- and mesopores in ultrastable Y zeolites but not the larger pores in beidellite. It explains why the beidellite catalyst is most stable in dodecane, the ultrastable Y zeolite catalyst in octane.

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