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Olefin oligomerization via zeolite catalysis

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Oligomerization of terminal and internal long-chain, linear olefins has been successfully demonstrated using large pore zeolites with high silica-to-alumina ratios as catalysts. Both reactant and product selectivities have been demonstrated using 12-membered ring zeolites for the oligomerization of C_{12}–C_{18} olefins. The catalytic activity of these zeolites decreases in the order faujasite > mordenite > pentasil; the activity of the Y-zeolites depends primarily upon the silica-to-alumina molar ratio, but not on the total acidity. 1-tetradecene oligomerization, followed by oligomer hydrogenation, yields synthetic lubricant base stocks with excellent physical characteristics.

Keywords: olefin oligomerization; large pore zeolites; synthetic lubricants

1. Introduction

Synthetic lubricant base stocks formulated around polyalpha-olefins (PAOs) are currently enjoying rapid market growth as automotive lube oil specifications get tougher and new restrictions regarding volatility, as well as low temperature requirements become harder to meet with conventional base stocks [1]. With synthetics, like the PAOs, low-viscosity, fuel-efficient engine oils can be formulated for extended service life, without compromising performance requirements.

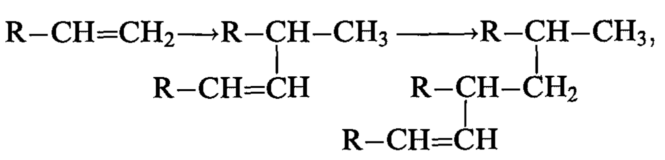
The chemistry of higher MW olefin oligomerization to form synthetic base stocks can be represented by the general equation

$$nC_mH_{2m} \longrightarrow C_{mn}H_{2mn}\,, \qquad (1)$$

where m defines the number of carbon atoms in the monoolefin substrate and n defines the number of monomer molecules reacting to form the product dimers, trimers, etc. The monoolefin substrate can be alpha or internal, linear or branched alkene. Reaction normally occurs sequentially. First the olefin monomer reacts with olefin monomer to form dimers, these dimers then react with additional olefin monomer to form trimers, and so on – illustrated here for 1-decene [2]:

$$2C_{10}H_{20} \longrightarrow C_{20}H_{40} \xrightarrow{C_{10}H_{20}} C_{30}H_{60}\,. \tag{2}$$

The oligomerization of olefins in the presence of zeolites is generally initiated by the Brønsted acid surface sites [3], consequently, the important properties of these zeolites include their Brønsted acid site density, the Brønsted acidity of said sites, as well as the accessibility of these acid sites. On the other hand, the degree of oligomer chain branching that occurs during the oligomerization process, illustrated schematically by



$$R{-}CH{=}CH_2 \longrightarrow \begin{array}{c} R{-}CH{-}CH_3 \\ | \\ R{-}CH{=}CH \end{array} \longrightarrow \begin{array}{c} R{-}CH{-}CH_3, \\ | \\ R{-}CH{-}CH_2 \\ | \\ R{-}CH{=}CH \end{array} \tag{3}$$

will depend upon the zeolite porosity, cage size, interconnecting channel structure, stacking faults, etc.

With regard to prior research dealing with higher MW olefin oligomerization via zeolite catalysis, Miller discovered that under certain conditions, medium pore size molecular sieves, such as ZSM-5 and crystalline metal silicates, are active for the oligomerization of C_{10}–C_{20} 1-alkenes [4]. Minachev et al. reported that the activity of a partially decationized zeolite, HKL, for higher MW alpha-olefins oligomerization depends on the amount of catalyst, but, does not depend upon the strength of Brønsted and Lewis acid sites [5]. Texaco has developed technology for the generation of higher MW olefin oligomers using boron trifluoride plus promoters [2,6,7] as well as acidified montmorillonite clays [8,11]. Higher MW α-olefin oligomerization is also known to be catalyzed by both transition metal salts and complexes (e.g. Ti, Zr and Ni) as well as other homogeneous and heterogeneous Lewis acids [3].

This paper deals with an improved process for the oligomerization of linear, C_{12}–C_{18} olefins, using zeolite catalysis – particularly zeolites with large pores and high silica-to-alumina ratios. High reactant and product selectivities have been demonstrated with 12-membered ring zeolites [12] useful for the oligomerization of C_{12}–C_{18} terminal and internal olefins. Oligomerization of these unsaturated oligomer products via hydrogenation gives excellent synthetic lubricant base stocks.

2. Experimental

Dealuminated Y-zeolites with varied silica-to-alumina mole ratios (SAR) of 6.5–60, including CP300-56 USY, CP304-37 SUSY, CP704-1 DAY, and CP301-26

VSUSY, were obtained from PQ Corp. in the form of fine powders or/and extrudates. A rare earth exchanged Y zeolite (SK-500), a ZSM-5 type zeolite (LZ-105) and silicalite (S-115) were obtained from Union Carbide. Also investigated in the present work were catalyst extrudates containing both S-115 and Y zeolites such as LZ-Y82 and LZ-Y20, which were custom made by Union Carbide. Mordenite samples including Zeolon 400H and 700H were provided by Norton Chemical. The binder material used in this work was alumina and/or silica–alumina. Montmorillonite acid-activated clays, such as Grade 24 used in the background study, were obtained from Engelhard Corp.

The zeolite catalyst samples were each tested for their initial activities in oligomerizing C_{12}–C_{18} olefins over a range of temperatures (140–300°C) in a batch reactor. In the batch-flask test, olefin and catalyst were charged to a three-neck flask equipped with a stirrer, thermometer, heating mantle, and a water-cooled condenser. The mixture was vigorously stirred and heated to a desired temperature for the desired time. The standard conditions used in the measurement of activities of zeolite-containing catalysts were: catalyst concentration, 10 wt%, 180°C; 4 h and 1-tetradecene. The mixture was then cooled to ambient temperature and filtered with suction. The liquid was analyzed for the monomer (M), dimer (D) and trimer plus heavier (T+) fractions by liquid chromatography.

The dealuminated Y-zeolites were also evaluated in the 100 cm^3, up-flow continuous reaction system at conditions: temperature, 140–200°C; pressure, 1.38–2.07 MPa; LHSV, 0.16–0.30. The oligomer products have been characterized, for the most part, via a combination of liquid chromatography, wet chemical analyses, and ^{13}C NMR.

3. Results and discussion

Our initial studies into the screening of various classes of zeolite structure [12] for the oligomerization of higher MW olefins involved the use of 1-tetradecene as the standard linear, alpha-olefin substrate. These batch experiments were conducted via the procedures described in the Experimental section. The results are summarized in tables 1 and 2 [13]. Over the temperature range considered (140–200°C), and about 0.1 MPa, we conclude the following points from these data:

(a) For the faujasite-class of zeolites (see table 1, ex. 1–4), increases in silica-to-alumina molar ratio lead to a parallel increase in both C_{14}-olefin conversion and in total oligomer formation. The ultrastable, dealuminated Y-zeolite, CP 301-26, for example, having the highest level of dealumination (table 1, ex. 1), provided the highest initial activity amongst the zeolite combinations screened. This result suggests that the oligomerization activity of the Y-zeolites depends primarily upon the acid strength of the zeolite sites [14], rather than upon the total number of Brønsted sites – since, for example, the total number of Brønsted sites of CP 300-56 USY is about 30-fold greater than that for CP 301-26 VSUSY. The crude oligomer prod-

Table 1
C_{14} alpha-olefin oligomerization – various faujasite, mordenite and pentasil[a] zeolites

Example	Catalyst description	Zeolite		C_{14} conv. (%)	Dimer (D)[b] (%)	Trimer (T)+ (%)	D/T+
		type	SiO_2/Al_2O_3				
1	CP301-26	Y	60	79.8	67.4	12.3	5.5
2	CP704-1	Y	40	77.9	68.0	9.8	6.9
3	CP304-37	Y	11	57.5	54.2	3.4	15.9
4	CP300-56	Y	6.5	41.9	36.0	4.9	7.4
5	SK-500	Re-Y	5.2	47.4	39.3	7.0	7.9
6	Zeolon 400H	mordenite	10	18.7	15.0	3.7	4.0
7	Zeolon 700H	mordenite	10	6.0	4.0	1.9	2.1
8	LZ-105	ZSM-5	240	<5.0	nd		
9	S-115	silicalite	370	<5.0	nd		

[a] Batch studies as described in Experimental, conditions: 180°C, 4 h.
[b] nd: not determined.

ucts are for the most part a mix of C_{14}-dimers, trimers, tetramers and pentamers, with minimal amounts of higher oligomers.

(b) Amongst the other classes of zeolites evaluated, the rare-earth exchanged Y-zeolite, SK-500, exhibited moderate activity (ex. 5), whereas both mordenite samples exhibited low conversions (ex. 6 and 7) and the pentasil, ZSM-5 type zeolite (LZ-105, ex. 8), or silicalite (S-115, ex. 9), proved nearly inactive for 1-tetradecene oligomerization under our test conditions. The order of activity appears, therefore, to be

Table 2
C_{14} alpha-olefin oligomerization – mixed zeolites[a]

Example	Catalyst description	C_{14} conv. (%)	Dimer (D) (%)	Trimer (T)+ (%)	D/T+
10	15% CP301-26 85% silica/alumina	80.2	60.3	19.8	3.0
11	20% CP304-37 80% silica/alumina	17.4	16.5	0	
12	60% S-115 20% LZ-Y82 20% alumina	11.8	10.5	0	
13	50% S-115 20% LZ-Y20 20% alumina 10% silica/alumina	30.7	25.8	4.9	5.3

[a] Batch studies as described in table 1.

$$\text{faujasite} > \text{mordenite} > \text{pensasil}. \tag{4}$$

(c) The ultrastable Y-zeolite, CP304-37, displays unexpected oligomer selectivity characteristics in that it gave an exceptionally high dimer/trimer ratio (ex. 3). This enhanced dimer selectivity might be due to diffusional considerations (reactant or product shape selectivity), or due to the nature of the oligomerization transition state within the zeolite matrix (i.e. restricted transition state selectivity [15]). In particular, the relative rates of 1-tetradecene isomerization versus oligomerization for CP 304-37 could lead to higher instantaneous concentrations of internal C_{14}-olefin that more slowly oligomerizes (vide infra).

We also briefly explored the possibilities of oligomerizing these same higher MW olefins with dual, or diluted, zeolite catalyst combinations (see table 2). Here, we find a small synergistic effect when employing, as catalyst extrudates, a mix comprising 15% CP 301-26 zeolite and 85% silica–alumina having the composition 84% SiO_2/16% alumina. This mix surprisingly gave olefin conversion levels slightly better, and product oligomer distributions with a higher trimer make, than neat CP 301-26 (cf. ex. 1 and 10). However, the pentasil-containing mixed zeolites (LZ-Y20 or S-115) still continued to exhibit low activities (ex. 12 and 13).

Data pertaining to the importance of olefin structure upon the oligomerization performance of the zeolite catalysts are summarized in table 3. For the most active, dealuminized Y-zeolite, CP 301-26, the reactivity for linear alpha-olefins follows the order:

$$\text{dodecene} > \text{tetradecene} > \text{hexadecene}. \tag{5}$$

Internal olefins are generally less reactive than the corresponding alpha-olefins of similar carbon numbers. The lower conversion of longer-chain olefins is likely due to the lower mobility of reactant and product molecules within the zeolite channels [16].

These data for zeolite-catalyzed olefin oligomerization may be compared with related studies carried out in our laboratories disclosing the effective use of certain acidic montmorillonite clays for oligomerizing long-chain olefins for synthetic base stock usage [9,10]. Performance summaries for Engelhard's Grade 13 and 24 clay catalysts (mineral acid-activated montmorillonite clays in powder, or 20/60

Table 3
$C_{12} \rightarrow C_{18}$ olefin oligomerizations – Y-zeolites [a]

Example	Ultrastable Y-zeolite catalyst	Olefin	Olefin conv. (%)	Dimer (D) (%)	Trimer (T)+ (%)	D/T+
14	CP301-26	C_{12} alpha	83.8	58.5	25.3	2.3
15	CP301-26	C_{16} alpha	74.1	56.1	18.0	3.1
16	CP301-26	C_{13} internal/C_{14} internal	51.4	47.4	4.1	11.6
17	CP301-26	C_{15} internal/C_{18} internal	56.7	50.6	6.2	8.2

[a] Batch studies as described in table 1.

mesh granular form, respectively) may be found in table 4. Again, where the olefin substrate is 1-tetradecene, or a mix of C_{13}–C_{16} internal olefins, we find higher oligomerization reactivity with the alpha-olefins,

$$\text{alpha olefins} > \text{internal olefins}\,, \tag{6}$$

although the conversion of the C_{13}–C_{14} internal olefins can be raised by increasing the reaction temperature (ex. 22). The treatment of the acidic Grade 24 granular clay with aluminum nitrate [10] improves the conversion of 1-tetradecene (ex. 23). This result implies that advantageous performance can be achieved by using a combination of Brønsted and Lewis acidity.

Comparing then the performances of the various zeolite-containing catalysts with the acidic clays, we conclude that generally:

- The zeolites give higher oligomer dimer-to-trimer (D/T+) ratios (up to 15.9 in table 1, ex. 3) – most likely because the oligomer products are branched in nature (eq. (3)) and the chain-length of the oligomers is limited by the pore openings.
- Only the 12-membered ring, ultrastable, dealuminated Y-zeolites provide comparable activity to the acidified montmorillonite clays (cf. tables 1 and 4).

1-tetradecene oligomerization over the diluted CP 301-26, i.e. ultrastable, dealuminated, Y-zeolite, CP316-26, 1/16″E, has also been successfully demonstrated in continuous unit equipment. Where oligomerization conditions are 155°C, 0.2 LHSV, we find over a 400+ hour test (see fig. 1) a moderate increase in dimer/trimer ratios and a moderate loss in catalyst activity (ca. 16% olefin conversion). These olefin conversion levels are, in fact, in the same range as those realized in our batch screening studies (table 1). The used catalyst extrudates show some carbonaceous deposits, but no gross changes in zeolite structure, or formation of fines [17].

Typical C_{14} α-olefin oligomer composite products, prepared as above, have been subsequently batch hydrogenated, in the presence of powdered nickel catalyst at 200°C [9], then filtered (to remove insoluble used catalyst) and stripped (to eliminate unreacted monomer). Typical composition and properties of a sample of hydrogenated 1-tetradecene oligomer mix are summarized in table 5. All properties are within the desired specifications, although a lower average dimer/trimer ratio for the composite oligomer would likely further improve the pour point (e.g.

Table 4
Olefin oligomerization – montmorillonite clays [a]

Ex.	Clay catalyst	Olefin	Operating temp (°C)	time (h)	Olefin conv. (%)	Dimer (D) (%)	Trimer (T)+ (%)	D/T+
18	Grade 13	C_{14} alpha	150	3	81.9	49.1	32.8	1.5
19	Grade 24	C_{14} alpha	150	4	92.4	43.9	48.4	0.9
20	Grade 24	C_{15}/C_{16} internal	150	4	45.6	33.7	11.8	2.9
21	Grade 24	C_{13}/C_{14} internal	150	4	63.5	45.7	17.7	2.6
22	Grade 24	C_{13}/C_{14} internal	180	4	78.0	51.1	26.9	1.9
23	$Al(NO_3)_3$/Grade 24	C_{14} alpha	160	5	85.0	45.2	39.8	1.1

[a] Batch studies as described in table 1.

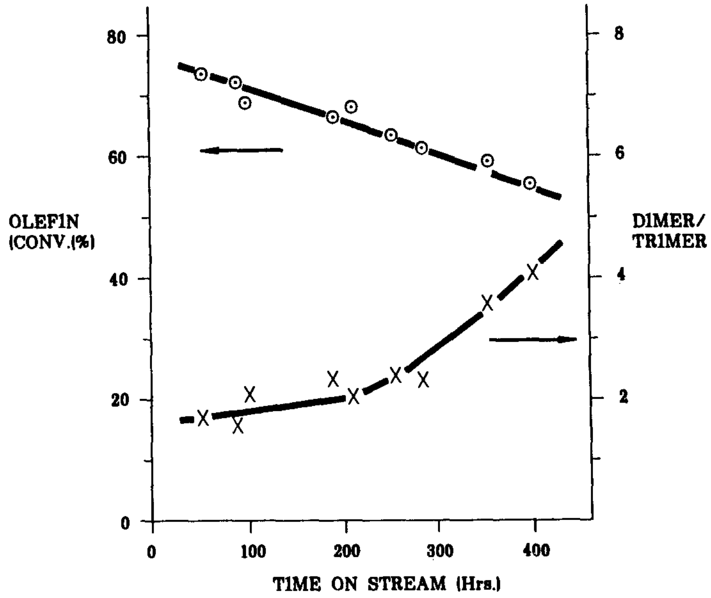


Fig. 1. 1-tetradecene oligomerization in continuous unit equipment as described in the Experimental section; catalyst, CP316-26; conditions, 155°C, LHSV 0.2.

< − 50°F). This type of synlube base stock has a uniform isoparaffin structure, similar to high quality paraffinic mineral base stocks, but superior performance in the areas of low temperature fluidity, improved viscosity indices and improved oxidative stability [2].

4. Conclusions

We conclude from this work that:

– Large pore, ultrastable, dealuminized Y-zeolites with high silica-to-alumina molar ratios are very effective solid acid catalysts for C_{12}–C_{18} olefin oligomerization. The oligomer products are excellent precursors for synthetic lubricant base stocks.

– Preferably, the solid acid zeolite catalyst should have a 12-member oxygen

Table 5
Typical hydrogenated 1-tetradecene oligomer

Composition (%)		*Properties*	
monomer	1.7	pour point	−30°F
dimer	58.5	viscosity	4.69 cSt (100°C)
trimer	29.6	viscosity index	125
tetramer	9.5	volatility	90.5% remaining at 233°C [a]

[a] Rate of heating: 10°C/min.

ring structure. Medium pore acidic zeolites, e.g. ZSM-5, are far less effective and the order of activity is faujasite > mordenite > pentasil.

– Even for the large pore Y-zeolites, which have low constraint indices (ca. 0.4 [15]), the order of olefin oligomerization activity is significantly influenced by substrate structure, viz. $C_{12} > C_{14} > C_{16}$ and alpha > internal. Presumably, oligomerization is limited to molecules with kinetic diameters $\leqslant$ ca. 7.4 Å [12].

– Certain ultrastable Y-zeolites, e.g. CP304-37, give oligomers with exceptionally high dimer / trimer ratios. This might be the result of higher instantaneous concentrations of internal olefin intermediate within the zeolite matrix.

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