

Shape-Selective Oligomerization of Alkenes to Near-Linear Hydrocarbons by Zeolite Catalysis

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Oligomerization results of propene, 1-decene, and isobutene catalyzed by zeolite HZSM-5 and zeolite HZSM-5 surface deactivated with 2,6-di-*tert*-butylpyridine show that faster oligomerization and a higher percentage of C₂₀⁺ products are obtained with the unmodified HZSM-5. Results of ¹³C NMR analysis show that when the oligomerization takes place inside ZSM-5 channels, the structures of the C₂₀⁺ products are nearly linear, with a small amount of methyl branching. A higher degree of methyl branching is obtained at higher reaction temperatures. The C₂₀⁺ products obtained from different olefins with surface-deactivated HZSM-5 under the same experimental conditions have nearly identical structures. The near-linear structure of the product indicates that when the oligomerization reaction takes place inside HZSM-5 channels, most of the alkyl substituents at the double bond of the olefins become part of the polymer chain, due to the steric requirement. When the surface acidity is unmodified, most oligomerization reaction takes place at the outer surface of the zeolite, and complex product structures result. © 1996 Academic Press, Inc.

INTRODUCTION

The classical acid-catalyzed cationic polymerization reactions of α -olefins, especially propene, have been investigated extensively (1–13). The polymerization reactions are usually accompanied by extensive isomerization, leading to products of an extremely complex structure (8–12). In contrast, olefin polymerization reactions catalyzed by Ziegler-Natta or other coordination catalysts result in head-to-tail addition of the monomer units (13–17),



and the polymers contain one alkyl branch per every second carbon atom in the main chain. Thus, for propene $R = \text{CH}_3$, and for 1-decene $R = n\text{-C}_8\text{H}_{17}$.

Oligomerization of propene using the shape-selective, medium-pore zeolite HZSM-5 has produced oligomers with a significantly less complex structure compared to

those from conventional acid catalysts (18–21). It has been proposed that polymerization on the catalyst surface, which is thought to resemble conventional acid catalysis, leads to more complex products than polymerization inside the catalyst channels. By modifying the surface acidity of HZSM-5 with 4-methylquinoline or hexamethyldisilazane (21) more linear products have been obtained in propene oligomerization, and, by modifying the surface acidity of HZSM-5 with 2,6-di-*tert*-butylpyridine (22), relatively linear oligomers have been obtained from oligomerization of propene and other olefins. By modifying the surface acidity of medium-pore zeolite HZSM-23 with 2,4,6-collidine (23, 24), substantially linear hydrocarbons were obtained in oligomerization of propene.

We have investigated the synthesis of C₂₀⁺ hydrocarbons (useful as lubricating oils) by oligomerization of lower olefins, using HZSM-5 as a catalyst. Oils with high viscosity indices (25) were obtained from propene, 1-decene, and isobutene using HZSM-5 surface modified with 2,6-di-*tert*-butylpyridine. The viscosity index (VI) is an empirical number, a widely used and accepted measure of the variation in kinematic viscosity due to changes in temperature between 313 and 373 K of a petroleum product. A higher VI value indicates a smaller decrease in kinematic viscosity with increasing temperature. VI is related to the structure of petroleum products, such that aromatics and cyclic aliphatics have lower VI values than aliphatics, and, among aliphatics, more linear structures have higher VI values. We examined the structures of oligomers with different VI values (after hydrogenation) by ¹³C NMR analysis and found that the high-VI oligomer products are aliphatics and are nearly linear in structure with relatively low degree of methyl branching.

EXPERIMENTAL

Propene and isobutene were Matheson c.p. grade. 1-Decene was 99% pure (Alfa) and was percolated through activated alumina before use.

The HZSM-5 catalyst (SiO₂/Al₂O₃ = 70) used in this work was a binder-free extrudate prepared in this labora-

¹ Deceased.

tory. We found, however, that in separate investigations of olefin oligomerization, Mobil's commercial HZSM-5 extrudate containing 65/35 wt% HZSM-5/ Al_2O_3 behaved similarly. HZSM-5 was surface deactivated with a sterically hindered base by stirring the zeolite in a 10% solution of 2,6-di-*tert*-butylpyridine (Aldrich, 97%) in hexane (~100 ml to 100 g catalyst) at room temperature for 2 h and then filtering and washing twice with hexane to remove the excess 2,6-di-*tert*-butylpyridine. After drying at room temperature to remove excess hexane, the catalyst was dried additionally at 383 K overnight. Elemental analysis showed that the catalyst contained 2.7% 2,6-di-*tert*-butylpyridine (or 0.1 mmol/g HZSM-5). 2,6-Di-*tert*-butylpyridine has a molecular size of $6.3 \times 8.0 \text{ \AA}$ which is too large to enter the medium pore ZSM-5 ($5.4 \times 5.6 \text{ \AA}$). The surface-modified HZSM-5 had the same diffusivity as the unmodified HZSM-5 when measured using 2,2-di-methylbutane: $D/r^2 = 3.5 \times 10^{-5} \text{ sec}^{-1}$ (26).

Oligomerization reactions were carried out in a Parr stirred autoclave (600 ml). HZSM-5, or HZSM-5 surface modified with 2,6-di-*tert*-butylpyridine, was used as the catalyst. The ratio of the catalyst to olefin was 1 g to 55 g. In each experiment, 5 g of a catalyst was charged into the Parr reactor. We found that when the 2,6-di-*tert*-butylpyridine-treated catalyst was used at 473 K in a Parr stirring reactor, no significant dissociation of the adsorbed 2,6-di-*tert*-butylpyridine took place, and essentially the same oligomerization results were obtained with or without the addition of 2,6-di-*tert*-butylpyridine to the olefin feed. However, when the reaction was carried out at 503 K, it was necessary to add 0.5 g 2,6-di-*tert*-butylpyridine to the olefin feed, as a lower-VI product was obtained without it. After flushing the reactor with nitrogen, 55 g liquid olefin was metered into the reactor. No solvent was used. The reactor was heated slowly to the reaction temperature while stirring and the pressure reached a maximum. A decrease in pressure was then recorded and was used as a measure of the olefin consumption. Each olefin was completely polymerized and liquid oligomer products were formed. Liquid samples were withdrawn from the reaction for product analysis by the GC method using a capillary column calibrated with hydrocarbon standards. The liquid products formed were generally not viscous and were easy to syringe, especially those from the reactions using the surface-modified catalyst. The product oils were distilled under vacuum to obtain the C_{20}^+ products. Each C_{20}^+ fraction was evaluated as a lubricant. The viscosities were measured at 373 and 313 K and the VI value was determined as described in ASTM D2270 (25). The C_{20}^+ fractions were dissolved in hexane, purged with nitrogen, and treated with hydrogen (45 psi) over 10% palladium on charcoal (Aldrich) in a Parr hydrogenator at ambient temperature until no more hydrogen was taken up. The hydrogenated oils were recovered by distillation and used for NMR examination.

^1H and ^{13}C NMR spectra were recorded with the JEOL FX 60Q, FX 90Q, and FX 270Q NMR spectrometers at their respective frequencies (^1H , ^{13}C , MHz): 60, 15; 90, 22.6; 270, 67.8. Limitations on instrument time required that most spectra be run under conditions of fairly rapid pulse repetition rate with nuclear Overhauser enhancement (NOE). A pulse repetition rate of 10.5 s was employed with a flip angle of 90° and complete proton decoupling (NOE). Since the longest T_1 in this work is 3.6 under conditions of air saturation, it can be calculated (27) that the largest error from the repetition rate- T_1 ratio is a loss of 5% in intensity. T_1 values were measured at 22.6 MHz and may differ slightly at 67.8 MHz. For molecules of the size discussed here, correlation times are less than $10 \times 10^{-10} \text{ s}$, and T_1 differences with frequency are not expected to be large. Contents of quaternary carbon atoms will be the most severely underestimated because of NOE differences.

The structures of the C_{20}^+ products were assigned based on model compounds and polymers (27-32).

RESULTS AND DISCUSSION

Table 1 compares the results of oligomerization of propene, 1-decene, and isobutene at 473 and 503 K catalyzed by HZSM-5 and by HZSM-5 surface modified with 2,6-di-*tert*-butylpyridine. The viscosities and VI values are given here to qualitatively indicate the molecular size and shape of the C_{20}^+ products. Generally, a lower viscosity indicates a lower molecular weight and a lower VI value indicates a more branched molecule. Table 1 shows that when the unmodified HZSM-5 is used as a catalyst, the amount of oil formed increases with the reaction time and reaches a plateau, and that the viscosity of the oil increases but the VI value decreases with the yield and with the reaction temperature. In addition, the viscosity continues to increase and VI continues to decrease after the oil yield has reached a plateau. In contrast, the surface-modified HZSM-5 under the same experimental conditions produces significantly less oil products. The product has a lower viscosity (lower molecular weight) and a significantly higher VI (a more linear structure) which does not decrease with the oil yield or with the reaction time. A lower VI is also obtained at a higher reaction temperature (473 vs 503 K). These observations clearly indicate a significant participation of the surface acidic sites in catalyzing the olefin oligomerization and isomerization of the products. When the unmodified HZSM-5 was used, the amount of C_{20}^+ products reached a plateau quickly, however. After that, the C_{20}^+ products underwent further polymerization and isomerization as indicated by the increase of viscosities (higher molecular weights) and the decrease in VI values (more branched structures). When the surface-modified HZSM-5 was used as the catalyst, the oligomerization occurred inside the zeolite channels.

TABLE 1
Effect of Reaction Temperature and Catalyst Surface Acidity on Oligomer Formation from Olefins

Olefin	Catalyst	Temp. (K)	Time (days)	C ₂₀ ⁺ Oil Yield (%) ^a	Kinematic viscosity 373 K cS	VI	
Propylene	HZSM-5	473	1.0	19.0	5.9	102	
			2.3	51.0	7.0	93	
			10.8	50.0	9.6	69	
	Surface inact. HZSM-5	473	3.0	41.2	6.9	46	
			3.0	5.6	3.5	157	
			7.1	10.4	4.0	165	
			11.8	17.1	4.0	163	
			503	1.1	12.4	3.5	127
				8.6	31.0	4.5	134
				10.9	32.0	4.7	133
1-Decene	HZSM-5	473	0.12	9.4	3.5	119	
			0.71	41.2	5.2	105	
			11.0	44.2	9.6	60	
	Surface inact. HZSM-5	473	17.7	33.3	4.3	154	
Isobutene	HZSM-5	473	6.0	33.8	6.1	66	
			503	4.9	32.7	9.2	50
			503	14.7	24.0	3.7	137

Note. Olefin/Catalyst = 100 ml/5 g.

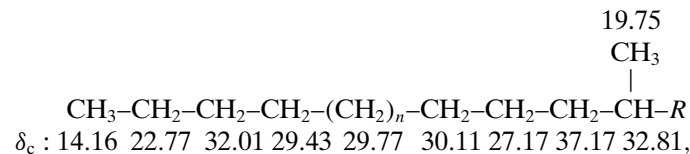
^a % of total products (C₂₀⁻ + C₂₀⁺); 100% olefin conversion.

Molecular rearrangement governed by the relative stability of carbenium intermediates cannot take place due to space limitation. The shape and size of the product were controlled by the space inside the channels and the ability of the products to diffuse in and out of the channels.

The use of the surface-modified HZSM-5 resulted in the production of oils with high VI value regardless of the feed olefin. The three olefins used have different structural features: propene is an α -olefin with a short methyl substituent at the double bond; 1-decene is an α -olefin with a long substituent at the double bond, and isobutene is a 1,1-disubstituted olefin. However, the VI values of oils in polymerization of propene and 1-decene at 473 K are similar (165 vs 154), and the VI values in polymerization of propene and isobutene at 503 K are also similar (134 vs 137). These observations indicate that when the surface acidic sites are absent, olefin oligomerizations were product shape selective.

The 50.1-MHz ¹³C NMR spectrum of the oil with the 93 VI product (propene polymerization catalyzed by HZSM-5 at 473 K) is compared with that of the oil with 165 VI (propene polymerization catalyzed by surface modified HZSM-5 at 473 K) in Fig. 1. Large differences in the types and quantities of alkyl branchings are apparent from the two spectra. The 93 VI product has substantial amounts of virtually every type of possible alkyl branching as tabulated in Table 2. Two qualitative features are apparent: (a) 1,2-enchaining of propene does not occur.

Isotactic polypropene (29) exhibits resonances for methyl (21.8 ppm), methylene (46.5 ppm), and methine (28.5 ppm) which are absent. Amorphous 1,2-enchained polypropene exhibits broad multiple resonances in the same regions (29); (b) The oil contains no long chain of uninterrupted methylenes. Methylene chains of short length are indicated by the multiple peaks near 30 ppm. In contrast, the predominant feature of the hydrogenated 165 VI product is that of a linear alkane with a low degree of methyl branching (δ_c = chemical shift):



where R is >C₄.

The level of methyl branching estimated from the ¹³C NMR spectrum is 4.3%, with minor amounts of propyl (0.7%) and ethyl (0.4%) branches, resulting in the 5.4% total branching. From the observed average carbon number of 26 obtained by the GC method, the total number of branches is 1.1 methyl branches per average molecule, 0.052 ethyl groups, and 0.06 propyl groups. Similarly, the 133 VI oil obtained from propene at 503 K has the same type of structure but has an average of 4.0 methyl branches per molecule (the average carbon number is 28). However,

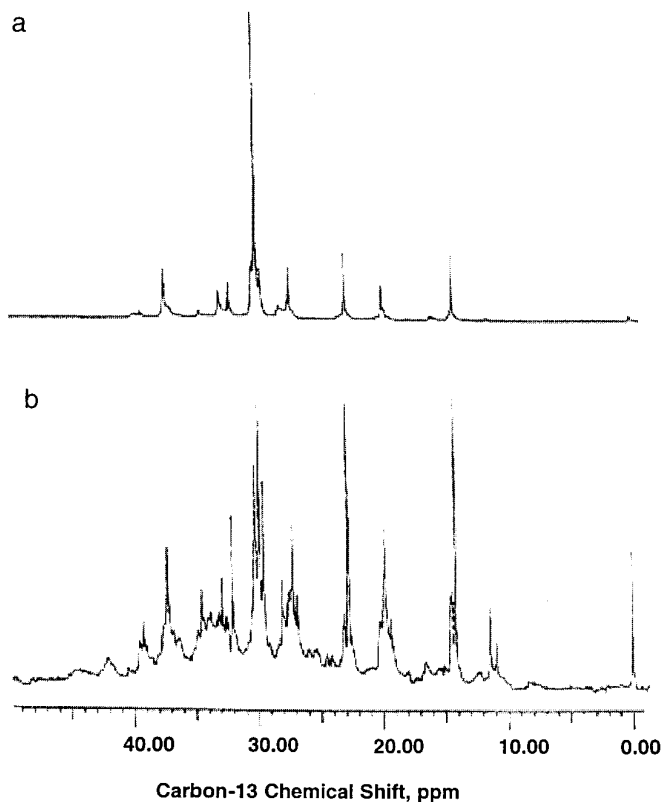


FIG. 1. 50.1-MHz ^{13}C NMR spectra of hydrogenated propene oligomers prepared at 473 K using (a) surface-modified HZSM-5; (b) unmodified HZSM-5.

TABLE 2

Methyl Groups in 93 VI Oligomer Product (^{13}C NMR at 67.8 MHz)

Type of methyl group	δ_c	% Area	No. C per molecule ^a
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{CH} \\ \\ \text{CH}_3 \end{array}$	22.75	3.4	0.82
$\begin{array}{c} -\text{CH}_2-\text{CH}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	21.6–18.7	9.0	2.16
$\begin{array}{c} -\text{CH}_2-\text{CH}-\text{CH} \\ \\ \text{CH}_3 \end{array}$	18.7–15.0	3.6	0.86
$\begin{array}{c} \text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ \text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$	14.61, 14.47	2.6	0.62
$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ and longer	14.17	3.3	0.79
$\text{CH}-\text{CH}_2-\text{CH}_3$	13.3–11.8	1.2	0.29
	11.8–0.0	2.6	0.62
$\text{C}-\text{CH}_2-\text{CH}_3$	7.6–8.8	0.4	0.10
Total		26.1	6.26

^a Based on vapor phase osmometry mol wt of 341: $\text{C}_{24}\text{H}_{50}$.

NMR analysis was not performed on the 137-VI oil obtained from isobutene at 503 K.

Although the 165 VI oil was obtained in low yield (17%), it is of special interest because it exemplifies what may be ultimately obtainable from olefin oligomerization by shape-selective zeolite catalysis. Its VI is very close to the structurally similar model compound 10-methyleicosane (33) which has a VI value of 163. At a higher temperature, oils of more methyl branchings are obtained but in higher yields.

The reactions of 1-decene and isobutene over HZSM-5 and surface-modified HZSM-5 gave similar results. High VI oils were produced using the surface modified HZSM-5 (Table 1). Figure 2 shows the ^{13}C NMR spectra of the oils from 1-decene using HZSM-5 (Fig. 2a) and surface-modified HZSM-5 (Fig. 2b). The carbon-13 spectra of the 154 VI oil from 1-decene (Fig. 2b) and the 165 VI oil from propene (Fig. 1a), obtained using the surface-modified HZSM-5, are nearly identical. The long alkyl chain ($n\text{-C}_8\text{H}_{17}$) character of 1-decene has been completely lost. The

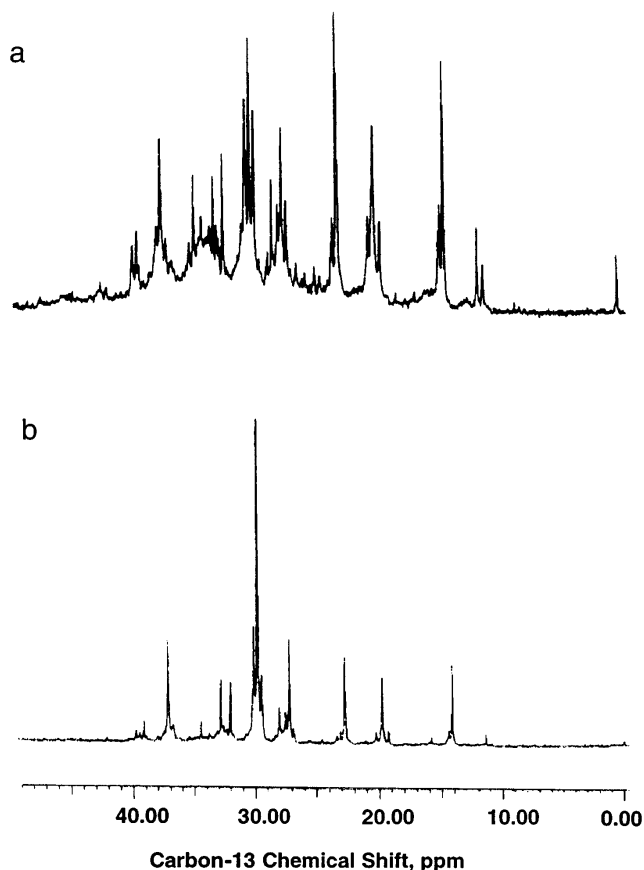
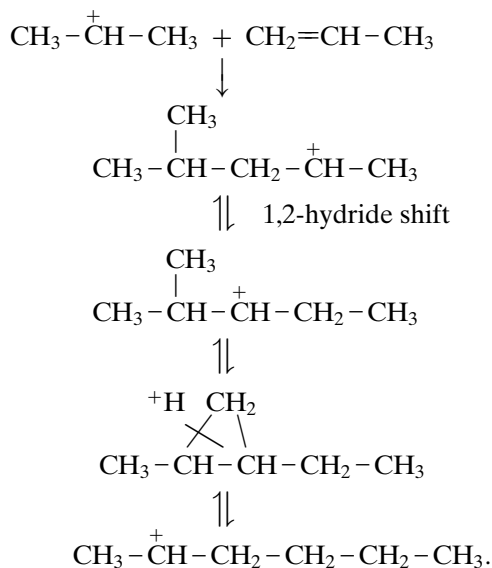


FIG. 2. 50.1-MHz ^{13}C NMR spectra of hydrogenated 1-decene oligomers prepared at 473 K using (a) unmodified HZSM-5; (b) surface-modified HZSM-5.

polymerization was product selective, independent of the feed olefin, when the surface-modified HZSM-5 was used as a catalyst. This contention is supported by the observations that (i) high VI oils were obtained from propene, 1-decene, and isobutene, and (ii) the ^{13}C NMR spectra of oils with similar high VI values produced from propene and 1-decene were nearly identical.

The production of a near-linear polyethylene-type material inside the zeolite channels from propene, 1-decene, and isobutene obviously involves skeletal rearrangement during the oligomerization. Formation of such products by cracking of oligomers to ethylene and subsequent polymerization of the ethylene is deemed unlikely. The temperatures used for the reactions are too low for appreciable cracking and the polymerization reactivity of ethylene is too small to compete with that of higher olefins (34, 35). A more likely route to the near-linear product structure is linearization via a series of carbenium rearrangements.

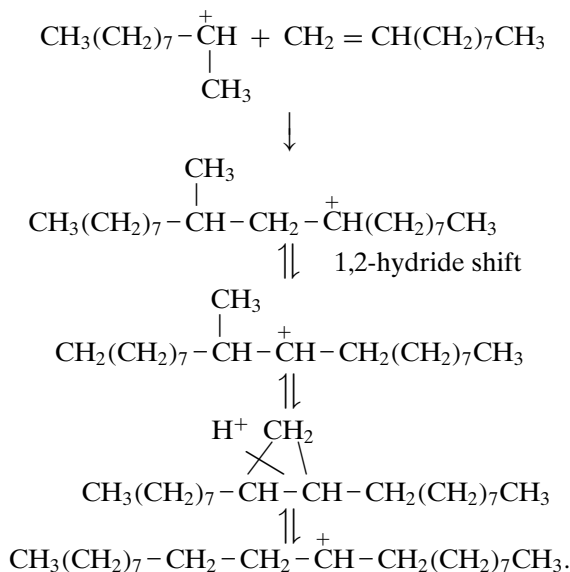
Van den Berg and co-workers (36) have observed that sorption of propene in HZSM-5 at room temperature resulted in the formation of linear oligomer. They have proposed a scheme for "stretching" reactions in the propene-HZSM-5 system, proceeding via protonated cyclopropyl intermediates,



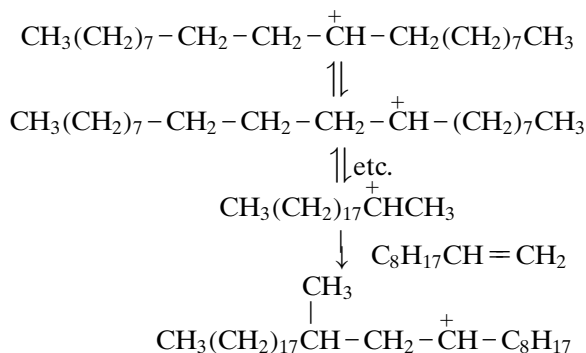
The process can be repeated at each propagation step resulting in a linear structure. Failure to linearize following propagation leaves a residual methyl branch.

Based on our results, we propose that higher olefins can react in a similar manner, losing methyl branches through the protonated cyclopropyl intermediate. Reactions of 1-decene and isobutene after the first formation of carbe-

nium from the olefin may be visualized for 1-decene as

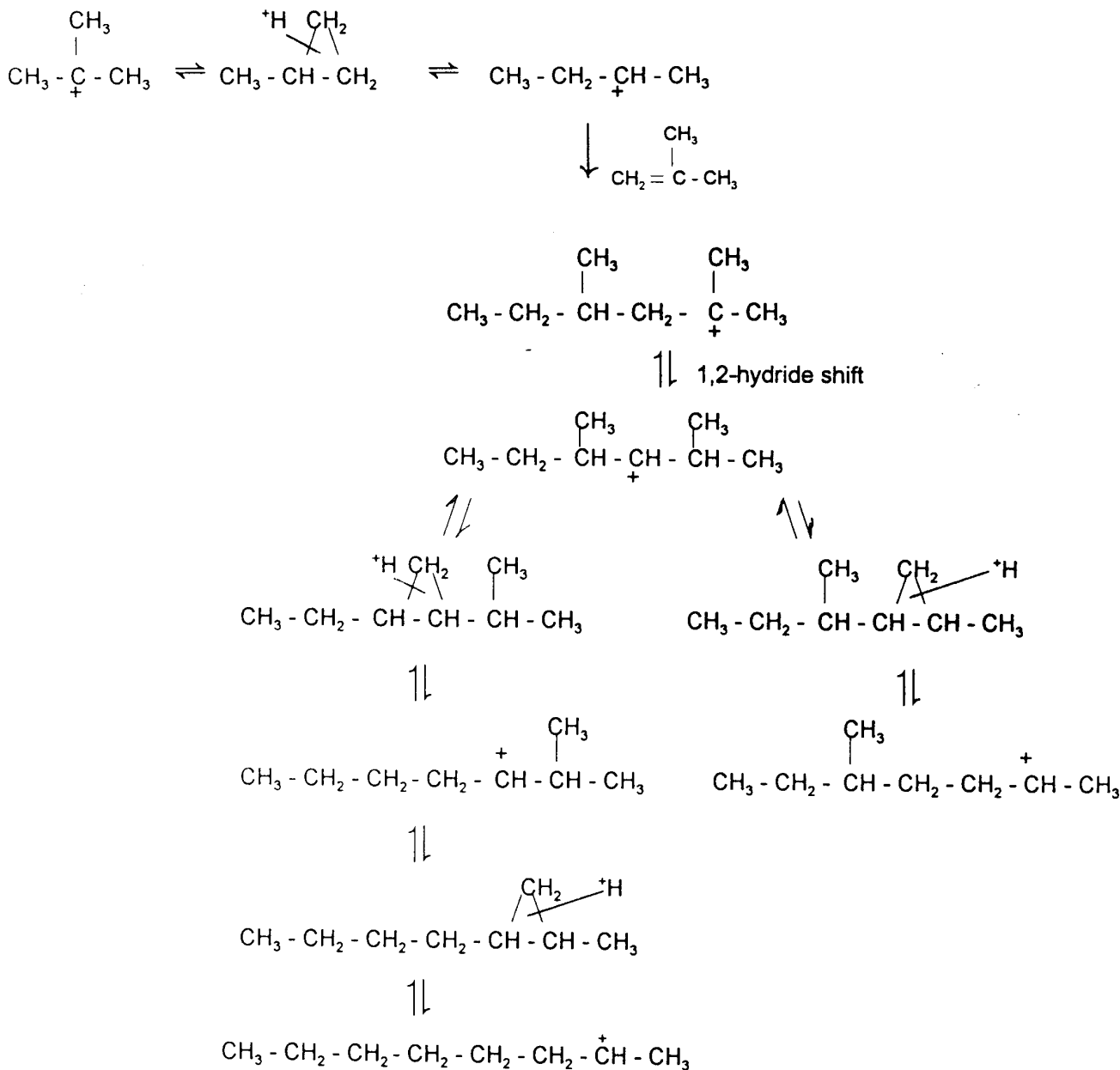


The resultant internal carbenium is restricted to react with monomer because of the 10-ring channel ($5.4 \times 5.6 \text{ \AA}$). The exception is at an intersection, however, such a T-shaped product would not diffuse out the channels. By a series of multiple 1,2-hydride shifts, the charge can migrate to the penultimate carbon, enabling the next propagation step.



The resultant carbenium may then lose a methyl branch by the protonated cyclopropane route, and the process can be repeated.

For isobutene, methyl insertion may proceed as described for propene. However, due to space restriction, the initial tertiary carbenium may rearrange to the less sterically hindered secondary carbenium before the addition of a monomer,



Propagation with monomer and skeletal rearrangement then continue.

CONCLUSION

Synthetic oils with high viscosity indices were produced in oligomerization of propene, 1-decene, and isobutene using HZSM-5 catalyst surface deactivated with 2,6-di-*tert*-butylpyridine. Under the same polymerization condition, oils with similar viscosity indices were obtained from different olefins (at 473 K: 165 VI from propene, 154 VI from 1-decene; at 503 K: 134 VI from propene, 137 VI from isobutene). ^{13}C NMR spectra show that the oils obtained using unmodified HZSM-5 have virtually

every type of possible branching. In contrast, oils obtained using surface-modified HZSM-5, after hydrogenation, have the predominant feature of a linear alkane with a low degree of methyl branching. The 165 VI (from propene) and the 154 VI (from 1-decene) oils prepared at 473 K are nearly identical. The product structure appears to be more dependent on the reaction temperature than the structure of the feed olefin. Conventional acid-catalyzed polymerization reactions of olefins are usually accompanied by isomerization leading to products with extensive branching. In stereospecific polymerization initiated by coordination catalysts, 1,2-enchainment takes place leading to head-to-tail polymers, and the original side groups in the monomer remain intact. When

the polymerization takes place inside ZSM-5 channels (e.g., the surface-modified HZSM-5), although acid catalyzed, nearly linear product structures are obtained. The product contains only small amount of methyl branchings even from a monomer with a long side group (1-decene). A mechanism for linearization is proposed. These results are of special interest because they exemplify what may be uniquely obtainable by shape-selective zeolite catalysis.

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