TRANSFORMATION OF 1-BUTENE OVER SYNTHETIC ZEOLITES*

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The behaviour of several zeolites as catalysts for the title reaction has been investigated by means of a continuous flow microreactor. Runs performed at atmospheric pressure indicated that at 423 K the completely protonic forms of the zeolites catalyze just the isomerization reaction. In the case of Y zeolites, oligomerization occurs only over the partially decationated samples, in the temperature range between 373 and 423 K and W/F between 0·2 and 22 $g_{cat}h/g_{1-but}$, to an extent which depends on the reaction conditions. Most of the catalysts were tested also under pressure (4·05 MPa) at 423 K. The protonic forms of Y and ZSM-5 zeolites seem promising catalysts in terms of both conversion and selectivity to oligomers. The 1-olefins account for 30% of the entire olefinic mixture. The octenes, which account for 70% of the liquid mixture, are mostly formed of dimethylhexenes. Trimers are also formed during the reaction and, in the very particular case of H[B]ZSM-5, tetramers are produced.

An interesting way to upgrade light olefins could be the selective oligomerization of n-butenes to octenes and dodecenes. Octenes are of commercial interest in the preparation of higher alcohols (e.g., nonanols) via hydroformylation, while dodecenes can be used to prepare alkylaromatics. 1-Butene dimerization over NiX zeolite has been studied in an early work by Forni et al.[1], who published also a list of references covering the patent literature. An updated review on this subject is found in ref.[2]. In these studies, as well as in the field of motor fuel production from light olefins, the catalytic tests are performed under pressure (few MPa) which thermodynamically favors higher hydrocarbons formation.

Most of the work concerning n-butenes transformation over zeolites at atmospheric or even subatmospheric pressure is directed to the investigation of the reaction mechanism. It is often based on the use of temperature programmed desorption or spectroscopic techniques[3-8], although flow reactors are also sometimes employed[3,9].

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While little or no doubts exist about the participation of hydroxyl groups in the isomerization of n-butene over acidic zeolites[3], some disagreement about the nature of sites involved in the further reactions of polymerization, cyclization, cracking, that the reactant can undergo over partially decationized zeolites, appears in the literature[4-7].

In the present work a continuous flow microreactor has been used to investigate the conversion of 1-butene over some acidic zeolites differing as to the structure (faujasites and pentasilicates), the degree of decationization (in Y zeolites) and the kind of T atom (in ZSM-5 type zeolites). In order to get an insight into the reaction pathway, the reaction was carried out under atmospheric pressure, testing the influence of the other reaction parameters (temperature, space-time and time-on-stream) on the relative extents of isomerization and the possible further n-butene reactions. The application point of view was considered by testing most of the catalyst also under pressure, to see if they could be useful in oligomerization processes of potential commercial interest.

EXPERIMENTAL

Materials and Catalysts

1-Butene (99·5% pure) was supplied by Praoil s.r.l.. Y zeolites were prepared from commercially available NaY powder cake (LZY-52 from Union Carbide). Four different decationized faujasites were obtained by the well known procedure: HNaY-17, HNaY-30, HNaY-55 and HNaY-98 (the figures indicate the % decationization degree with respect to the original Na content). ZSM-5 and Boralite catalysts were prepared according to the patents of Argauer and Landolt[10] and Taramasso et al.[11], respectively.

Apparatus, Procedure and Analysis

The activity comparison runs at atmospheric pressure were always carried out on fresh catalyst samples, in a continuous fixed bed quartz microreactor. The runs at 1·52 and 4·05 MPa were performed in a fixed bed stainless steel reactor. Figure 1 shows the scheme of the apparatus.

Before each run the catalyst was activated in situ overnight under nitrogen flow at 773 K. After cooling down to the chosen reaction temperature, the nitrogen flow was stopped and the pure hydrocarbon was fed.

The reactor effluent was analyzed on-line on a FID gas chromatograph equipped with a Hewlett–Packard fused-silica capillary column (length 50 m; I.D. 0·20 mm), coated with cross-linked Ultra 1. The other operating conditions were as follows: carrier gas H_2, 1 ml/min, split ratio 200 and volume of the injection capillary 100 µl. The oven temperature program was: 313 K maintained for four minutes, heating at 15 K/min up to 423 K and then at isotherm conditions for five minutes. Some GC/MS analysis of the condensed reaction mixture were also performed on a 5890A Hewlett–Packard gas chromatograph, connected with a 800 Finnigan ITD detector, for a better identification of the reaction products. In order to determine the double bond position in the olefinic chain, in some cases the spectra of ^1H and ^{13}C species were also recorded by means of a VXR 300 VARIAN NMR-spectrometer (7·05 T).

RESULTS AND DISCUSSION

Atmospheric Pressure Runs

The results of the catalytic runs performed at 423 K on the protonic forms of the structurally different zeolites are reported in Table I. The catalytic activity is expressed in terms of reactant mole % conversion *C*, and wt. % composition of the products mixture. As it can be seen, after 1 h on stream at space time $W/F = 1{\cdot}4\ g_{cat}h/g_{1-but}$ the conversion is very high over each catalyst and the product mixture is composed by 2-butene (*cis* and *trans*) with trace amounts of C_8 hydrocarbons. The isomerization of 1-butene is practically the only reaction occurring on these catalysts also at higher *W*/*F* values. No conversion at all was observed at the same temperature and $W/F = 3{\cdot}3\ g_{cat}h/g_{1-but}$ over the NaY and HNaY-17 samples, while the more decationized Y zeolites (HNaY-30 and HNaY-55) gave the results reported in Table I. 2-Butene is by far the most abundant product in both cases

TABLE I

Catalytic activity at atmospheric pressure after 1 h on-stream

Catalyst	*T* K	*W*/*F* $g_{cat}\cdot h/g_{1-but}$	*C* mole %	Products distribution, wt. %							
				C_3	i-C_4	C_{4-2}	C_5	C_6	C_7	C_8	C_9+
HNaY-98	423	1·4	88	0·1	tr	99·2	0·2	—	—	0·5	—
H[Al]ZSM-5	423	1·4	83	0·10	—	99·2	0·3	—	—	0·4	—
l-H[Al]ZSM-5	423	1·4	90	—	—	99·4	—	—	—	0·6	—
H[B]ZSM-5	423	1·4	17	—	—	98·9	—	—	—	1·1	—
HNaY-30	423	3·3	89	0·11	0·30	77·38	0·67	1·57	2·13	15·48	2·36
HNaY-55	423	3·3	92	0·26	0·96	66·91	2·39	2·20	4·90	18·83	2·73

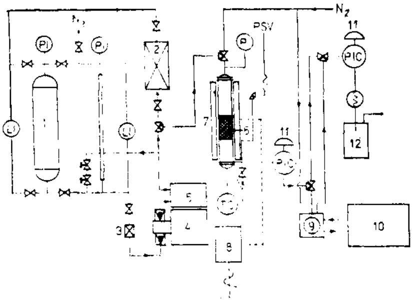


FIG. 1

Scheme of the apparatus. 1 Feed reservoir, 2 feed dryer, 3 pump filter, 4 pump, 5 pump controller, 6 reactor, 7 furnace, 8 temperature controller, 9 sampling valve, 10 gas-chromatograph, 11 Groove valve, 12 collecting trap, LI level indicator, PI pressure indicator, PIC pressure controller but some other hydrocarbons are also present in the reactor effluent. Their nature is olefinic, the only paraffin revealed in significant amounts being isobutane. It is worth noticing that moderate amounts of C_8 olefins (mainly dimethylhexenes) are formed over HNaY-30 and HNaY-55, revealing the occurrence of the dimerization reaction to some extent.

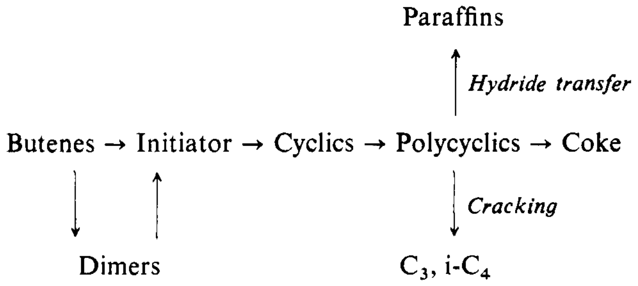
The influence of the W/F value on the catalytic behaviour of HNaY-55 has been also tested. After 1 h on stream at 423 K and $W/F = 0{\cdot}2\ g_{cat}h/g_{1-but}$, just 33 mole % of 1-butene was converted, but when W/F was raised to 1·4, the conversion reached 92% and kept this high level for W/F values up to 22. In this range the composition of the product has changed as shown in Fig. 2. At very low W/F, 2-butene forms almost exclusively. As W/F increases, C_8 olefins rapidly grow, reach a maximum and then smoothly decrease while the total amount of the other olefins in the C_5-C_9 range continuously increases with increasing W/F. Propene is always formed to a very low extent and a very slight increase of isobutane is observed.

Conversion and products distribution depend also on temperature. HNaY-55 gave 38% 1-butene conversion at 373 K, 92% at 423 K and 90% at 573 K (after 1 h on stream, $W/F = 1{\cdot}4\ g_{cat}h/g_{1-but}$). As Fig. 3 shows, the higher the temperature, the higher the formation of C_5-C_9 hydrocarbons, except C_8 olefins. The latter appear in the highest amount when the reaction temperature has an intermediate value. 2-Butene is practically the only product at 373 K and never decreases under 82% with increasing temperature. A slight increase of propene and isobutane yield both present in low concentration, seems to occur as temperature increases.

A decrease in the catalytic activity was the rule for all the catalysts tested, which appeared to be coloured after the run, from pale yellow to brown, depending on time-on-stream and temperature. However, they could be easily regenerated by heating in air flow at 773 K. Thus, the conversion level of HNaY-30 passed from the initial value of 89% (first hour on stream), to 83% (second hour) and was 82% after 3 h. At the same time the composition of the product was found to change with time-on-stream as shown in Fig. 4. A sudden decrease in the amount of C_8 olefins and a smoother diminishing of C_5-C_7 and C_9 hydrocarbons occur simultaneously with a marked increase of 2-butene production. Very similar change of the product distribution were observed over HNaY-55.

On the basis of the product distribution reported above, some considerations can be advanced, concerning the competing reactions in the system. As already stated, the presence of C_8 olefins besides 2-butene isomers indicates that the oligomerization reaction occurs simultaneously with 1-butene isomerization. Propene can be taken as a measure of the cracking activity of the catalyst, while isobutane is assumed to come from cracking plus hydride transfer, rather than from skeletal isomerization of the linear butenes, according to Langner[9]. This author investigated the transformation of 1-butene over a partially decationized Y zeolite at higher temperatures and reported the formation of high amounts of propene and isobutane.

His results agree with the general reaction (Scheme 1).



SCHEME 1

The so-called initiator, which is thought to be formed either from the butenes or from the dimers and is supposed to have a dienic structure, can start the cyclization

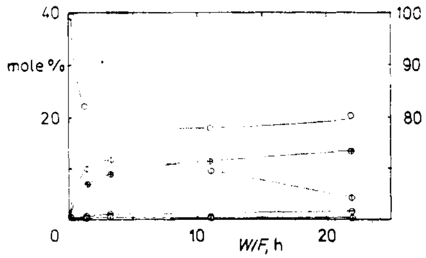


FIG. 2

Composition (mole %) of the product vs W/F for HNaY-55 at 423 K and atmospheric pressure. ○ C_{4-2}; ◎ C_3; ⊖ i-C_4; ⦶ C_8; ⊕ $C_5 + C_6 + C_7 + C_9$

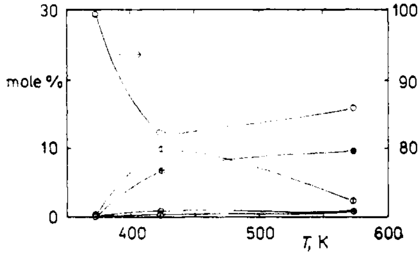


FIG. 3

Composition (mole %) of the product vs temperature for HNaY-55 at $W/F = 1{\cdot}4$ and atmospheric pressure. ○ C_{4-2}; ⊙ C_3; ⊖ i-C_4; ⦶ C_8; ⊕ $C_5 + C_6 + C_7 + C_9$

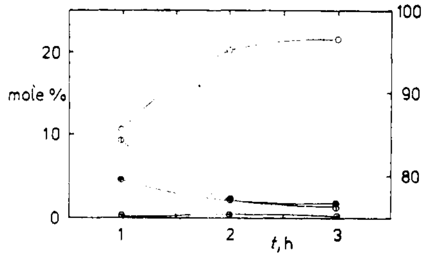


FIG. 4

Composition (mole %) of the product vs time-on-stream for HNaY-30 at 423 K, $W/F = 3{\cdot}3$ and atmospheric pressure. ○ C_{4-2}; ⊙ C_3; ⊖ i-C_4; ○ C_8; ⊕ $C_5 + C_6 + C_7 + C_9$

reaction by undergoing a Diels–Alder reaction with olefins. The observed cracking products should be formed from the cyclic hydrocarbons.

In our case, over HNaY-30 and HNaY-55 zeolites very little propene and isobutane are formed. Although this latter is seen to increase slightly with W/F and temperature, other paraffins are almost absent. Moreover, the yellow-brownish colour of the catalyst after the reaction seems to indicate a low aromaticity of the coke. Accordingly, it can be concluded that cracking to gaseous hydrocarbons and hydrogen transfer occur always to a very limited extent and this would mean in turn that just the early steps of the above scheme can take place under our mild experimental conditions.

Thus, 1-butene double bond isomerization is the predominant reaction and it becomes further favoured as time-on-stream increases and the catalyst deactivates (Fig. 4). The sites where the latter reaction occurs seem therefore more involved in the deactivation process, likely because of the formation and strong adsorption of polymeric material. This possibility is consistent with the observed formation of $C_5 - C_7$ and C_9 olefins: they could come from the partial fragmentation of these adsorbed species, which would prefer this route over the cyclization to "aromatic coke". At this light an increase of this fragmentation with W/F and temperature should be expected. Figs 2 and 3 show that this really happens, the simultaneous decrease in C_8 production being an indication that the dimers also are unstable under more stressed reaction conditions.

In the preceding part the 1-butene conversion to 2-butenes has been called isomerization for brevity. More precisely it is the simultaneous occurrence of both double bond shift and geometrical isomerization that leads to the mixture of n--butenes. It is generally accepted that over acidic zeolites these transformations involve a common carbenium ion intermediate, the secondary butyl carbenium ion[12]. The hydroxyl groups vibrating at 3 650 cm^{-1} and assigned to O_1H groups are reported to be the active sites for the reaction[3]. Jacobs et al.[3] observed over HY rapid 1-butene isomerization to 2-butenes, which were preferentially adsorbed causing catalyst deactivation. Hydrogen-deficient polymeric deposits were detected on the catalyst by IR technique and some of the supercage hydroxyl groups vibrating at 3 650 cm^{-1} were found to be involved irreversibly in this process. The concentration of residual hydroxyl groups was considered responsible for the continued activity although the possibility that the polymeric residue could act as an active intermediate in butene isomerization, behaving as a proton donor, was also discussed.

At this light the observed inactivity of our NaY and HNaY-17 samples is not surprising, due to the absence or too low concentration of OH groups. In these cases just the adsorption of 1-butene is likely to occur, according to literature[4,6] on Na^+ sites. On the basis of IR results obtained for similar systems[6], we can assume that on the HNaY-30 catalyst, the presence of hydroxyl groups should be significant and could induce 1-butene adsorption through hydrogen bond formation, thus initiating the process of carbenium ion formation which can lead to the isomerization products. Besides these latter products, also dimers were formed, although in moderate amounts (Table I). They also should originate from a carbenium ion intermediate, as it is well known that oligomerization reactions of the olefins can be explained by the classical carbonium ion theory[13]. This is directly supported by the above cited I.R. study[6], which indicated the involvement of O_1H hydroxyls in the oligomer formation over partially decationized Y zeolites.

Moreover, it is commonly accepted that double bond shift and geometrical isomerization of ight olefins occur readily on weak acid sites while oligomerization requires stronger acidity[13]. On this basis it could appear surprising that no oligomerization occurs over our HNaY-98, i.e. over the sample where both the concentration of OH groups and the acid strength are at the highest level. It should be noted also that none of the fully protonated zeolites of Table I, independently of their structure, is able to catalyze the production of C_8 olefins.

The possibility of increasing dimerization over these catalysts at higher temperatures was tested on H[Al]ZSM-5. At 573 K and $W/F = 1{\cdot}4\ g_{cat}h/g_{1-but}$ conversion was almost complete (96%), as expected; 1-butene isomerization is very limited (11·5% by weight of 2-butenes in the product mixture), while the amounts of propene and isobutane (9·8 and 8·6%, respectively) pointed to a remarkable cracking activity, indicated also by the significant presence of paraffins. Despite the moderate production of C_8 hydrocarbons (10·0%), oligomerization does not appear to be enhanced, as GC/MS analysis revealed the predominant aromatic character of this cut, and also of the C_7 and C_9 fractions (20·9 and 13·4%).

Both isomerization and oligomerization require carbenium ion formation. Apart from the above cited differences concerning the necessary acid strength, it should also be noticed that while the first reaction is unimolecular, oligomerization needs the presence of butene molecules adsorbed on catalyst sites adjacent to the centres where the carbenium ion is formed. Adsorption can occur on Na^+ ions as well as on O_1H hydroxyls but in this latter case the adsorbed species interacts with the carbenium ion, while this cannot occur on the alkali-metal ions. The ratio between the number of merely adsorbing sites and true proton donor centres of appropriate strength should therefore play a fundamental role in determining the selectivity towards oligomerization. If this ratio is too low, the catalyst possesses a high carboniogenic activity but the lack of unprotonated adsorbed butene molecules makes oligomerization unlikely.

An evaluation of this ratio was tried. Surface acidity of HNaY-55 and HNaY-98 was determined by titration with 1-butylamine in anhydrous solvent. Due to the molecular sizes of the indicators used, it is likely that this technique is suitable for measuring the number of acid sites of the supercage only, i.e. those active in butene conversion. The corresponding results (expressed as mmol of titrating base/g of catalyst) are reported in Table II. As for the number of Na^+ ions located in supercage positions we can refer to the XRD study of Gallezot and Imelik[14] on Y samples having the following formula: $Na_{26.6}H_{29.4}Y$ and $Na_{2.2}H_{53.8}Y$. These authors found that 47% of the Na^+ ions of the first zeolite were in S_{II} sites, while this fraction was 37% in the second sample. As these zeolites are very similar to our HNaY-55 and HNaY-98 (see Table II), we can assume that the same distribution holds also for our samples and thus calculate the amount of Na^+ ions present in supercage positions in each case. This amount is reported in Table II, expressed as mmol of Na^+/g of catalyst. By dividing it by the sum of acid sites of intermediate ($-1{\cdot}5 \leqq H_0 \leqq 3{\cdot}2$) and high ($H_0 \leqq -1{\cdot}5$) strength, i.e. the amount of those acid centres which can be reasonably assumed as involved in oligomerization, the values of 1·5 and 0·2 are obtained for HNaY-55 and HNaY-98 samples, respectively. Although merely indicative, these values appear to be consistent with the proposed picture: oligomerization is possible over HNaY-55 as there are about 3 sites able to supply butene molecules for every 2 sites of appropriate acidity, but it cannot occur over HNaY-98.

High Pressure Runs

The present zeolite catalysts have been investigated also under 4·05 MPa, at 432 K and $W/F = 1\ g_{cat}h/g_{1-but}$. Several hours on stream were needed to reach steady state conditions. Conversion values corresponding to this situation (time-on-stream $\geqq 7{\cdot}5$ h) are reported in Table III, together with the composition of the mixture of the reaction products, grouped according to their carbon number, as usual. From a thermodynamic point of view, high pressure favors high molecular weight products, and this effect is seen in Table III: over each catalyst the reactant was transformed to a good extent and, besides *cis* and *trans* 2-butene, C_8, C_{12} and even heavier hydrocarbons were formed. No aromatics were present in the product,

TABLE II

Chemical composition and surface acidity of Y zeolites

Catalyst	Chemical Formula	Surface acidity, mmol/g cat.			Na^+ amount in supercage positions mmol/g cat.
		$H_0 \leqq -1{\cdot}5$	$-1{\cdot}5 \leqq H_0 \leqq 3{\cdot}2$	$3{\cdot}2 \leqq H_0 \leqq 6{\cdot}8$	
HNaY-55	$H_{30}Na_{25}Y$	0	0 65	0·81	0·94
HNaY-98	$H_{54}Na_1Y$	0·13	0·87	1·00	0·19

which was composed almost exclusively of olefins (paraffins to olefins ratio always $\leqq 0{\cdot}05$).

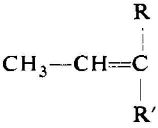
Some interesting considerations can be drawn by the examination of the NMR spectra of the reaction product obtained over the HNaY-98 sample. By comparing the proton spectrum of Fig. 5 with reference standard, one can conclude that the occurrence of the multiplet between 5·70 and 5·82 ppm is related to the presence of a $-CH=$ group, while the multiplet between 4·76 and 4·95 ppm is attributed to the terminal $CH_2=$ group of a 1-olefin. The peaks between 4·95 and 5·4 ppm were attributed to $R-CH=CH-R$ olefins. From the evaluation of the peak intensities it is possible to state that about 30% of the liquid olefins in the reaction mixture are 1-olefins (error within 5%).

These assignments were confirmed by the ^{13}C spectra (^1H coupled and decoupled, Fig. 6), which point to the absence of aromatics. Under this situation the signals at fields lower than 136 ppm can only be attributed to the $CH_2=$ group of terminal olefins. The most significant and abundant signals (*) and the related attributions are the following:

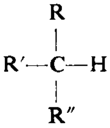
*140·35 ppm $CH_2{=}CH{-}CH_2{-}R$ (1-olefins)

*125·80 ppm $R{-}CH{=}CH{-}R'$ (with branched R and R′)

*124·51 ppm $R{-}CH_2{-}CH{=}CH{-}CH_2{-}R'$ (linear olefins in the double bond field)

*117·77 ppm 
$CH_3{-}CH{=}C(R)(R')$ (branched 2-olefins)

*113·18 ppm $CH_2{=}CH{-}CH_2{-}R$ (1-olefins)

*44·83 ppm 
$R'{-}C(R)(R''){-}H$

Concerning faujasites, a comparison between the specific behavior of HNaY-30 and HNaY-98 seems interesting. For the sake of completeness, these zeolites have been tested also at 152 MPa and at atmospheric pressure (423 K and $W/F = 1\ g_{cat}h/g_{1-but}$) and the whole set of data has been collected in Fig. 7, where the oligomerization activity (measured by the amount (%) of liquids in the products mixture) is reported vs pressure. As it can be seen, the effect of pressure on HNaY-98 is straightforward: the catalyst, which was unable to give oligomerization under atmospheric pressure, produces appreciable amounts of dimers and trimers at 1·52 MPa and this activity is further enhanced at 4·05 MPa. The moderate oligomerization observed at atmospheric pressure over HNaY-30 increases as the pressure is raised to 1·52 MPa, while it changes very slightly between 1·52 and 4·05 MPa. Under the latter condi-

TABLE III

Catalytic activity at 4·05 MPa, 423 K and $W/F = 1\ g_{cat}h/g_{1-but}$, time-on-stream 7·5 h

Catalyst	C mole %	Product distribution, wt. %								
		C_{4-2}	C_5	C_6	C_7	C_8	C_9+	C_{12}	$C_{12}+$	light
HNaY-30	71	53·65	0·19	0·43	0·50	26·29	3·92	12·92	1·44	0·66
HNaY-98	89	53·31	0·17	0·48	0·21	29·97	3·60	11·50	0·20	0·56
H[Al]ZSM-5	42	71·80	—	—	—	5·65	0·18	12·81	8·92	0·64
1-H[Al]ZSM-5	75	78·68	—	—	—	14·04	0·55	6·37	—	0·36
H[B]ZSM-5	53	48·49	—	—	—	9·50	—	13·13	28·48	0·40

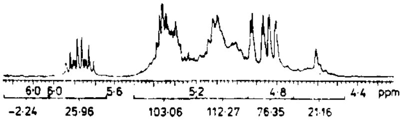


FIG. 5

Proton spectrum of the liquid hydrocarbons from HNaY-98

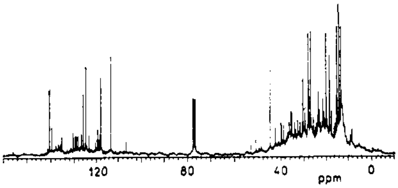


FIG. 6

Carbon-13 spectrum of the liquid hydrocarbons from HNaY-98

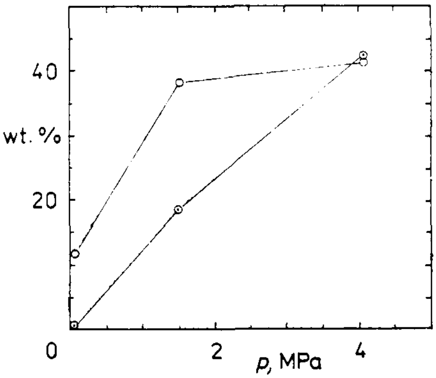


FIG. 7

Amount (wt.%) of liquid hydrocarbons vs pressure (p, MPa) at 423 K and $W/F = 1{\cdot}0$. ○ HNaY-30; ⊙ HNaY-98 tions the oligomerization activity is practically independent of the degree of decationization of the zeolite, being the same over HNaY-30 and HNaY-98.

At 423 K and atmospheric pressure both reactant and products are in vapor phase. Thus, if oligomerization occurs really through the interaction between adsorbed n-butene molecules and the carbenium ion formed on the acid sites, the presence of Na^+ ions is of crucial importance. On the contrary, at 4·05 MPa and 423 K the reaction products are in liquid phase and the reactant itself is just above the condensation point (critical temperature 419·5 K, critical pressure 4·02 MPa). This means that the internal voids of the catalyst particles are completely filled by the liquid products and the particles themselves are surrounded by a liquid film; as a consequence, the reactant would contact the catalyst only after dissolution into the liquid. Under these conditions Na^+ ions do not play any particular role, the situation being very similar to liquid-phase oligomerization.

A detailed comparison between the various catalysts of Table III is meaningless under such conditions. Nevertheless, some remarks can be formulated. It appears from Table III that the faujasitic zeolites catalyze oligomerization reactions to a higher extent than do the pentasilic H[Al]ZSM-5 and 1H[Al]ZSM-5, as indicated by the lower total amount of C_8, C_{12} and higher olefins present in the product mixture formed over these latter catalysts. No significant differences in the distribution of the C_8 isomers were found between Y and ZSM type zeolites, this cut being composed mainly by dimethylhexenes ($\geqq 90\%$) in both cases. It seems therefore that shape selectivity effects do not intervene in determining the isomer distribution, which appears to be the one expected on the basis of true oligomer formation. However some cracking with consecutive random cooligomerization seems to occur over H[Al]ZSM-5, as indicated by the formation of heavy olefins ($> C_{12}$) with continuous distribution of carbon numbers. These latter products are completely absent in the case of 1H[Al]ZSM-5, which differs from H[Al]ZSM-5 as to the Si/Al ratio and the crystallite size. Both this two parameters could be responsible for the observed differences in the oligomers distribution but even a temptative evaluation of their relative weight seems hazardous, due to the particular reaction conditions. However, it is worth noticing that in the case of 1H[Al]ZSM-5 the very small cristallite dimensions ($\leqq 0{\cdot}005$ μm) make very unlikely the occurrence of cracking of oligomers with consecutive random cooligomerization, as intraparticle diffusional restrictions should be less compelling.

The comparison between H[B]ZSM-5, H[Al]ZSM-5 and 1H[Al]ZSM-5 deserves attention. Boralites are usually reported to be less active than [Al]ZSM-5 in the catalysis of several reactions, due to their weaker acidity[15–22]. Our results seem in line with this general finding: although the reactant conversion attained under quasi-stationary conditions is comparable over H[B]ZSM-5 and [HA]ZSM-5 (Table III), they differ considerably as to the initial activity. This is shown in Fig. 8 where conversion is plotted vs time-on-stream for the pentasilic catalysts: after of

3 h it is about 50% in the case of H[B]ZSM-5 and 93% for H[Al]ZSM-5. The source of catalytic activity of boralites is still questioned but a correlation with the amount of residual framework Al has been reported for several reactions[19,20]. With our pentasilic catalysts we can observe that H[Al]ZSM-5 has the highest Al content (Si/Al = 15) and therefore the highest number of acid sites (and thus a very high conversion); however, these sites do not seem very long living, as the conversion drops to 42% after a few hours on stream. 1H[Al]ZSM-5 has practically the same initial conversion of H[Al]ZSM-5, but its activity decrease is smoother and a stable conversion level slightly higher than 70% is quickly attained. This would indicate a higher site efficiency, as expected on the basis of the Si/Al value (250). The highest site efficiency is reached in 1H[Al]ZSM-5 where the presence of just 500 ppm of residual framework Al enables the catalyst to convert 50% of 1-butene with a stable trend.

Furthermore it should be mentioned that according to Andersen et al.[15] variously treated boralites were inactive towards high pressure propene oligomerization below 573 K, while aluminous HZSM-5 catalyzed the reaction to a good extent under the same conditions. At higher temperature boralite was active but the presence of boron did not influence the product distribution, which showed an almost continuous spectrum in the C_6-C_{18} range. On the contrary, in our case a striking difference between boralite and the two aluminous HZSM-5 catalysts concerns the oligomers distribution: although the formation of reaction products heavier than dimers is expected over H[B]ZSM-5 according to the cristallite size (0·02 μm, one order of magnitude higher than for 1H[Al]ZSM-5) it is surprising that they are exclusively represented by C_{16} olefins, as if just a true tetramer formation could occur simultaneously with dimerization and trimerization. This unique feature of H[B]ZSM-5 seems to be promising from the point of application; the catalyst is worth of further investigation.

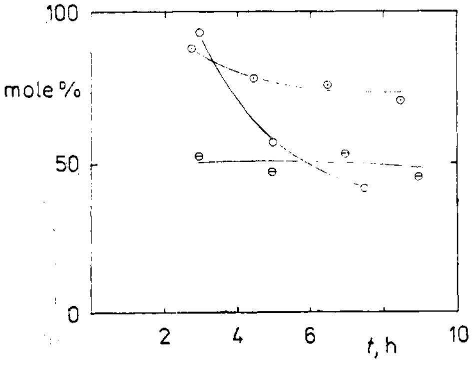


FIG. 8

Conversion (mole %) vs time-on-stream (t, h) at 4·05 MPa, 423 K and $W/F = 1{\cdot}0$. ○ H[Al]ZSM-5; ⊙ 1-H[Al]ZSM-5; ⊖ H[B]-ZSM-5

CONCLUSIONS

Besides the considerations concerning the reaction mechanism some conclusions of practical importance can be drawn from this work. Under 4·05 MPa and 423 K, HNaY-98 and 1-HZSM-5 seem to be promising catalysts in terms of both conversion and selectivity to oligomers. The 1-olefins account for 30% of the entire olefinic mixture. The octenes, which account for 70% of the liquid mixture, are mostly formed of dimethylexenes. Trimers are formed during the reaction and, in the very particular case of H[B]ZSM-5, also tetramers are produced.

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