ISOMERIZATION AND HYDROCRACKING OF N C10 - N C17 ALKANES ON Pt/H-BETA

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ABSTRACT

Long chain paraffins ranging from decane to heptadecane are hydroconverted over Pt loaded H-BETA. The isomerization-hydrocracking products are analysed using high resolution capillary GLC and compared with those obtained with Pt/H-USY and Pt/H-ZSM-5. Pt/H-BETA behaves as an ideal bifunctional catalyst and its main characteristics are a high selectivity for isomerization, pure primary cracking of the hydrocarbon chain and reduced propane formation. In contrast to zeolite Y, the pores of zeolite-BETA restrict the formation of ethyl- or bulkier side chains in the feed isomers.

INTRODUCTION

During the last decade zeolite research has focussed on the synthesis of high-silica zeolites and the investigation of their properties. Among them the Pentasil family of materials received particular attention. Other high-silica zeolites were known before the advent of the Pentasil zeolites but have been overlooked. Zeolite BETA is such a zeolite.

Zeolite BETA was synthesized in 1967 by Mobil researchers [1] and showed a silica to alumina ratio in the range from 5 to 100 [2]. It is an aluminosilicate crystallised from a gel containing tetra-ethylammonium (TEA) or Na ions [1,2] and eventually Cr, Fe or La [4]. The XRD peaks can be indexed in a cubic unit cell with a_0 = 1.204 nm [1] although Breck [5] contests this. The zeolite has a pore volume of 0.20 ml g^{-1}, sorbs hexane and cyclohexane and can be dealuminated by HCl treatment [3]. Recently it was shown that the void structure was similar to that of zeolite L and consists of pores with 12-membered rings and lobes [6].

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Only a few industrial applications of this zeolite have been claimed till today. It is able to alkylate benzene with dodecene to prepare phenyldodecanes [8]. In this reaction it has a selectivity similar to that of zeolite L, ZSM-4, ZSM-20, ZSM-38 and mazzite [8]. It can also be used for the formation of diphenylmethane out of benzene and trioxane [7]. High-silica BETA loaded with platinum is an efficient dewaxing catalyst avoiding extensive gas formation [9]. Dealuminated-BETA seems to have potential uses as a catalyst component in the hydrocracking-dewaxing of heavy oils [10].

In the present work, it was aimed to investigate more fundamentally the potential of zeolite BETA in isomerization-hydrocracking reactions of n-paraffins. Its behaviour was compared to that of proven bifunctional catalysts as Pt/H-ZSM-5 and Pt/Ultrastable Y (US-Y).

EXPERIMENTAL

For the synthesis of zeolite BETA a mixture of tetra-ethyl orthosilicate (80 g) and a 40 % aqueous solution of TEA-OH (56.4 g) was stirred for 1 hour to achieve complete hydrolysis of the ester. Then were subsequently added : $Al(NO_3)_3.9H_2O$ (9.5 g), NaOH (1.4 g), TEA-OH solution (56.4 g) and water (8.1 g) under continuous stirring. The gel obtained (with Si/Al = 15) was autoclaved at 393 K. After rotation for 6 days zeolite BETA with Si/Al = 14 was formed in the autoclave. The sample showed the typical XRD-spectrum [2] and a crystal size of 0.2 μm. The H-form of this zeolite was obtained after washing, calcination at 723 K, NH_4-exchange and heating at 673 K.

H-BETA showed a hydroxyl spectrum with bands at 3725 and 3600 cm^{-1}. Similar spectra were reported for H-ZSM-5 samples [11]. The Pt-H-form of BETA was prepared upon impregnating the NH_4-form with aqueous $Pt(NH_3)_4Cl_2$, drying, calcination in oxygen and reduction in hydrogen at 637 K. The latter two treatments were performed in situ in a continuous flow tubular reactor after pelletizing the Pt/NH_4-zeolite into 0.3-0.5 mm grains. The reactor could be operated up to 2 M Pa. Paraffins and hydrogen were mixed in a thermostatted saturator. The whole conversion range was covered by varying the reaction temperature. The reactor outlet was analyzed on-line over a 50 m CPt Sil 5 fused silica column using temperature programming between 283 and 473 K.

The reference zeolite Pt-US-Y was prepared by repeated steaming from NH_4-Y [12]. ZSM-5 with Si/Al = 60 and crystal dimensions of 1-4 μm was synthesized and transformed into a bifunctional catalyst according to published methods [15]. All catalysts contain 1 % by weight of platinum.

RESULTS AND DISCUSSION

1. Isomerization and hydrocracking of tridecane

As a typical example the isomerization of tridecane into mono- and dibranched feed isomers and its hydrocracking is shown in Fig. 1 for the three zeolite frameworks, BETA, ZSM-5 and US-Y. In comparable conditions BETA is more active than ZSM-5 because it contains a higher number of Brønsted sites (the Si/Al ratio of the samples is 14 and 60, respectively). As also found for n-C10 [15], ZSM-5 is more active than US-Y. As far as overall selectivity is considered, BETA behaves as US-Y and from the figure the following reaction sequence is obvious :

tridecane → monobranched C_{13} isomers → dibranched C_{13} isomers → cracked products
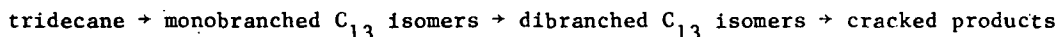
As reported for various n-paraffins on Pt loaded US-Y [12], CaY [14] and dealuminated Y [15], very high selectivity for isomerization was also observed for BETA. In terms of a classical bifunctional mechanism, an increase in isomerization selectivity has to be associated with a decrease in average acid strength [14].
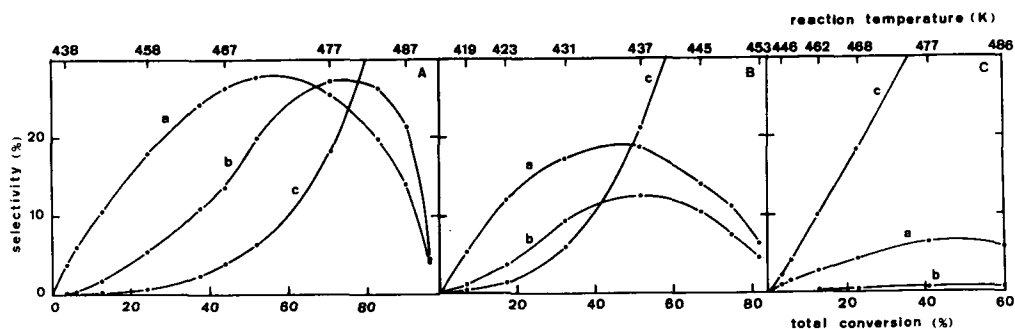

Fig. 1. Conversion of $n-C_{13}$ into mono- (a), dibranched (b) isomers and cracked products (c) against its total conversion; $P_{tridecane}$ = 1.3 k Pa; P_{H2} = 2 M Pa; A, Pt/H-BETA (WHSV = 0.88 h^{-1}); B, Pt/H-US-Y (WHSV = 0.47 h^{-1}); C, Pt/H-ZSM-5 (WHSV = 0.88 h^{-1})

A high selectivity for dibranched isomers is reached on BETA (Fig. 1). The degree of branching of the feed isomers is not determined by acid strength but rather by the size of the zeolite pores [6]. The high yield of dibranched isomers on BETA suggests that this zeolite contains no constraints for the formation of highly branched intermediates. The high overall selectivity for isomerization against hydrocracking also suggests that BETA doesnot possess the very strong acid sites of ZSM-5.

2. Composition of the feed isomers

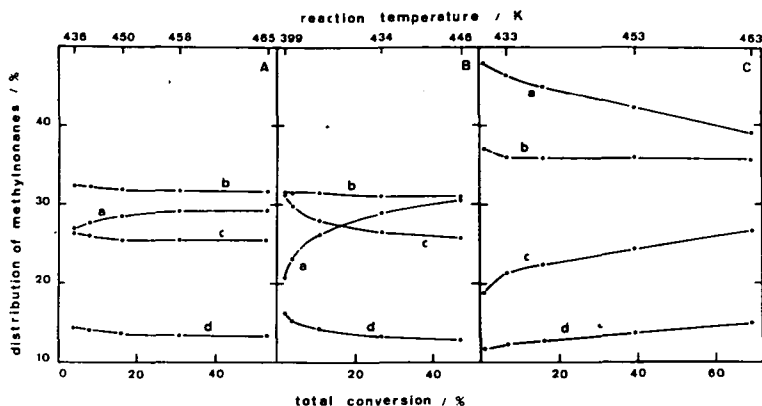Starting with n-decane as feed, the distribution of the methyl-branched isomers is shown in Fig. 2.

Fig. 2. Distribution of the methylnonanes at increasing total conversion of decane at P_{decane} = 1.1 k Pa, P_{H2} = 0.1 M Pa; A, Pt/H-BETA at WHSV = 0.4 h^{-1}, B, Pt/US-Y at WHSV = 0.2 h^{-1} and C, Pt/H-ZSM-5 at WHSV = 0.3 h^{-1}; a, 2-methylnonane, b, 3-methyl-, c, 4-methyl- and d, 5-methylnonane.

The behaviour of US-Y has already been described at this level [13] : the formation of 2-methylnonane is kinetically hindered since branching occurs via protonated cyclopropane (PCP) intermediates, the rate of formation of which is lower near the end of a hydrocarbon chain [14]. From medium conversion on, thermodynamic equilibrium is reached. In ZSM-5 an excess of 2-methylnonane is found at low conversions, largely at the expense of the 4- and 5-methylisomer. This composition gradually changes to that of equilibrium. Such behaviour is typical for small crystal ZSM-5 [16], while for large crystals the initial composition is not affected by the degree of conversion [15]. Transition state shape selectivity [15] may be responsible for this behaviour.

The distribution of these isomers in BETA is close to that observed on US-Y zeolite, although the kinetic hindrance of 2-methylnonane is less pronounced. This indicates that PCP-type branching is followed by very rapid equilibration via methylshifts. When the Brønsted sites are very diluted in an open zeolite framework, it has been reported that the relative rates of isomerization by alkyl-shifts drops considerably compared to PCP-branching [16]. The behaviour of BETA is explained in this context by its high aluminium content, although secondary isomerization at the external surface cannot be entirely excluded.

The distribution of the isomers at the maximum isomerization conversion in terms of methyl-, ethyl- and propyl-branched products is shown in Table 1. On ZSM-5 only methyl-isomers are formed, which confirms previous reports [15,16] and which can be ascribed to transition and/or product shape selectivity. The product distribution on BETA and US-Y is rather similar, although less propyl- and ethyl-branched isomers are formed on the former zeolite.

Table 1

Distribution of monobranched isomerization products on Pt/H-zeolites

at maximum isomerization conversion

Feed	Zeolite	WHSV/ h^{-1}	Temp. K	Isomerization %	Isomer distribution %		
					methyl	ethyl	propyl branched
nC_{10} [a]	BETA	0.4	472	42	88.5	10.2	1.3
	US-Y	0.2	446	34	86.0	12.3	1.7
	ZSM-5	0.3	453	30	98.8	1.2	0.0
nC_{17} [b]	BETA	0.9	472	28	87.6[c]	12.4	-[d]
	US-Y	0.6	431	19	85.1[c]	14.9	-[d]

a, P_{H2} = 0.1 M Pa and P_{C10} = 1.1 k Pa; b, P_{H2} = 2 M Pa and P_{C17} = 0.9 k Pa; C, including 3-ethylpentadecane; d, propyltetradecanes, butyltridecanes and pentyldodecane are not resolved from the dibranched isomers.

This indicates that BETA is a large pore zeolite with cages or lobes slightly smaller than the supercage of the faujasite structure. This is confirmed when other isomer or product fractions are considered. Indeed, the yield of methyl-ethylbranched C_{10} isomers in the dibranched ones amounts to 4.5 and 1 % for US-Y and BETA, respectively.

3. Carbon number distribution of hydrocracked products

On large pore zeolites in the acid form with a well-dispersed metal phase on it, ideal bifunctional cracking is expected. This cracking consists of primary events and consequently the carbon number fractions are distributed symmetrically among their carbon numbers. Central scission is preferred in this type of chemistry and propane abstraction is not very probable [6]. On medium pore zeolites, central scission is less abundant and propane formation has increased [6,15,16]. The carbon number distribution of the hydrocracked products from decane, dodecane and tridecane at low cracking conversions are given in Fig. 3 for the three zeolites to illustrate this.
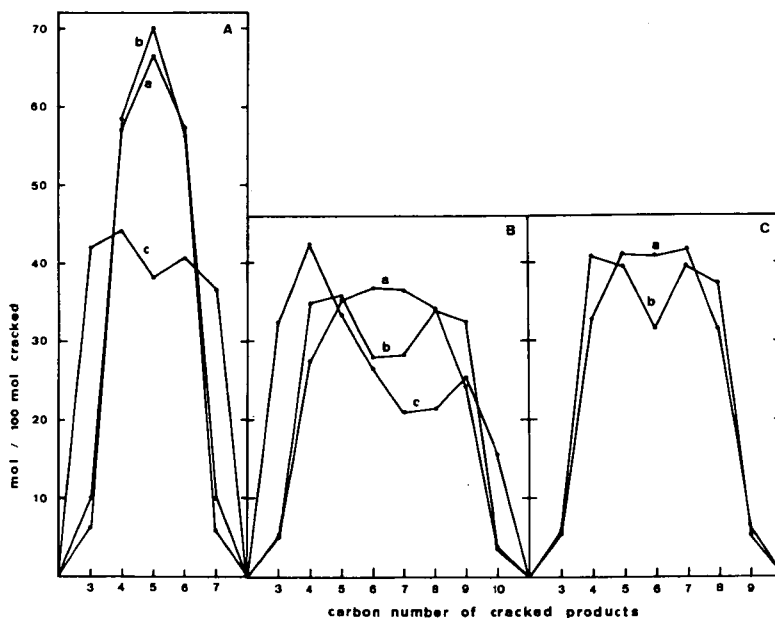

Fig. 3. Carbon number distribution of hydrocracked products from decane (A), dodecane (C) and tridecane (B) at 5 % hydrocracking over a, US-Y, b, BETA and c, ZSM-5 zeolites. Experimental conditions for tridecane and decane are given in Figs. 1 and 2, respectively; for dodecane : P_{C12} = 1.2 k Pa; P_{H2} = 2.0 M Pa; on BETA, WHSV = 0.5 h^{-1} at 465 K, and on US-Y, WHSV = 0.4 h^{-1} at 434 K.

The typical features mentioned are observed for US-Y with each feed molecule. On ZSM-5, much propane is formed, central scission is decreased and secondary cracking of the longer hydrocracked products occurs mainly for the longer feed molecules. This confirms earlier work [6,15,16]. The cracking of decane on BETA shows the ideal pattern. Central scission is even more preferred than over US-Y and propane abstraction is lower. With C_{12} and C_{13} paraffins as feed, however, minor but significant differences between BETA and US-Y appear : the preference of central scission has decreased over BETA. It will be shown elsewhere that mainly A-type cracking of α,α,γ-tri-branched isomers is responsible for this central scission [18]. The absence of dimethylethylisomers in BETA, as a result of shape selective hindrance, can explain that central scission decreases with increasing carbon number of the feed [18]

4. Product distribution in the individual carbon number fractions

The composition of the C6 carbon number fraction is shown in Fig. 4 for feed paraffins with carbon number between 10 and 17. At low cracking conversions it is seen that over US-Y as well as over BETA this composition is the same irrespective of the chain length of the feed hydrocarbon.
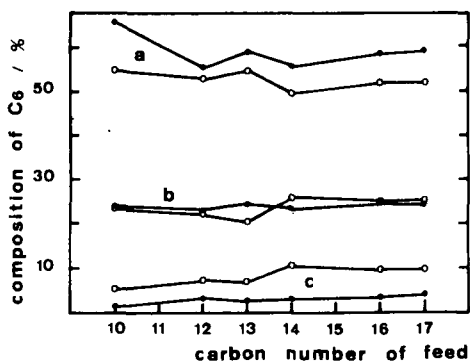

Fig. 4. Composition of the C6 carbon number fraction against the feed carbon number at 5 % hydrocracking conversion over US-Y (full points) and BETA (open points). Experimental conditions : for C10, C12, C13 : Fig. 3; C17 : Table 1; for C14 : P_{H2} = 2M Pa, P_{C14}= 1.1 k Pa, WHSV = 0.6 h^{-1} on BETA at 444 K and 0.4 h^{-1} at 425 K on US-Y; for C16 : pressures as for C14, WHSV = 1.0 h^{-1} at 490 K on BETA and WHSV = 0.5 h^{-1} at 436 K US-Y; a = 2-methylpentane; b = 3-methylpentane; c = 2,3-dimethylbutane.

The figure shows that on both zeolites this composition is not dependent on the chain length of the feedstock. Such a behaviour is only possible when the discrete β-scission mechanisms operate on the parent carbocations at a rate which is not dependent on their chain length. Furthermore, also the relative concentration of these cations with a structure susceptible to an attack by one of the scission mechanisms is independent of the feed. This behaviour will be explained in detail in a later publication. The slight differences in the 2-methylpentane and 2,3-dimethylbutane yields over BETA and US-Y are the result of slight differences in the feed isomer composition mainly at the level of the ethyl- and propyl-branchings.

For the C4 and C5 fractions the same constant composition of the fraction, irrespective of the carbon number of the feed was observed. The yield of isobutane in the C4 fraction varied between 80 and 86 % and between 78 and 83 % for BETA and US-Y, respectively. Isopentane represented always 85 to 89 % of the C5 fraction over BETA and 83 to 87 % over US-Y.

The composition of the C7 fraction hardly changes for feeds longer than C10. The decreased yield in n-fragments in the fraction obtained by propane abstraction is indeed a typical feature of ideal hydrocracking [19] in large pore zeolites and consequently the constant composition is only observed now from C11 on as feed. A typical difference between BETA and US-Y is the decreased yield of ethylpentane on the former zeolite. This component can only be obtained from ethyl-branched parent ions which are less abundant in BETA.

These observations are of key importance for the design of dewaxing and hydrocracking catalysts. It follows that whatever mixture of long chain paraffins is cracked over zeolites as US-Y and BETA always almost identical compositions of the hydrocracked products will be obtained.

CONCLUSIONS

In this work it is shown that zeolite Pt/H-BETA shows all the characteristics of an ideal bifunctional isomerization and hydrocracking catalyst when long chain n-paraffins are used as feed. This material is very active and selective for isomerization of such feeds. Once bulkier than methyl-branchings are formed, sterical restrictions are imposed by the inner structure of this zeolite. This behaviour distinguishes the BETA structure from that of ultrastable Y.

The yields of the carbon number fractions of the hydrocracked products in BETA ressemble those obtained over US-Y. The low yield of ethyl-branchings in the multiply-branched feed isomers causes a somewhat reduced rate of central scission on zeolite BETA. Finally, the distribution of the individual isomers in each carbon number fraction is very similar in BETA and US-Y.

ACKNOWLEDGMENT

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