Adsorption of C_8-hydrocarbons, potential intermediates of skeletal isomerisation of *n*-butene, in the 10-membered ring zeolite

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Adsorption of various octenes and octanes was studied with a 10-membered ring molecular sieve, H-[B]ZSM-5. Adsorption of octane was very fast, the double-branched octane diffused slowly, and the triple-branched molecules could not enter the channels of the sample. Since the 10-membered ring molecular sieves are the best catalysts for skeletal isomerisation of *n*-butene, trimethylpentenes or other larger oligomers cannot be intermediates in this reaction. By contrast, skeletal isomerisation of *n*-butane which is known to require 12-membered ring channels, can involve a trimethylpentane-like molecule as an intermediate.

Keywords: adsorption, skeletal isomerisation, *n*-butene, *n*-butane, octane

1. Introduction

Due to more strict environmental laws, branched ethers like MTBE will become an important part of motor gasoline. Since the availability of isobutene is limiting the MTBE synthesis, both main routes of isobutene production – skeletal isomerisation of *n*-butene and of *n*-butane – have enjoyed an increasing popularity in the last years. The mechanisms of these isomerisations are still being discussed, and one can speak of two groups of possible mechanisms: (a) monomolecular and (b) bimolecular ones.

The bimolecular mechanism for skeletal isomerisation of *n*-butene (or *n*-butane) is expected to proceed via dimerisation of butene to C_8-carbenium ion, which isomerises and is selectively cracked to isobutene [1]. With regards to the *n*-butene reaction by this mechanism, two main ideas have been put forward. Mooiweer et al. [2] suggested that two molecules of *n*-butene dimerise to 3,4-dimethylhexene, which isomerises to 2,4-dimethylhexene. This octene can crack to one molecule of isobutene and one molecule of *n*-butene. The second route suggested proceeds via trimethylpentenes [3]. With this mechanism, one molecule of isobutene reacts with *n*-butene to 2,2,3-trimethylpentene, which should isomerise to 2,4,4-trimethylpentene. Thereafter, 2,4,4-trimethylpentene should be selectively cracked to two molecules of isobutene. On the first glance, forgetting for a moment the size of the molecules, this mechanism seems to be the more probable one, since it runs via a tertiary carbenium ion, which is more stable than the secondary one.

Recently, a new, so-called pseudomonomolecular mechanism has been suggested [4]. The reaction scheme is very similar to the mechanism via trimethylpentenes. The authors of ref. [4] suggest that *n*-butene molecule reacts with an immobilised tertiary carbenium ion, firmly anchored in the surface, instead of reacting with isobutene from the gas phase.

All mechanisms of skeletal isomerisation suggested for *n*-butene can be, in principle, also applied to skeletal isomerisation of *n*-butane. Compared to butene isomerisation, there is only a very small difference, because dehydrogenation of butane to butene is generally considered to be the first step of skeletal isomerisation anyway [5].

All microporous materials, used with most success for skeletal isomerisation of *n*-butene to isobutene, are 10-membered ring molecular sieves – ferrierite [2], SAPO 11 [6], MnAPO 11 [7], ZSM-22 [8] and ZSM-23 [9]. A study comparing 8-, 10- and 12-membered ring molecular sieves clearly showed that no other microporous materials can be used with equal success [10]. The 8-membered ring zeolites do not allow the transport of isobutene in the pores and the 12-membered ring zeolites possess a very low stability and selectivity.

However, in contrast to *n*-butene, the skeletal isomerisation of *n*-butane to isobutane requires 12-membered ring zeolites or open surfaces. In this respect, the most often used microporous materials are mordenite [11] and zeolite beta [11]. A comparison of 10- and 12-membered ring zeolites (for example SAPO 11 and SAPO 31 [12]) showed a lower activity of materials with the smaller pores. This indicates that the prevailing mechanism is different for *n*-butane and *n*-butene.

If pore diameter is so crucial for the skeletal isomerisation of *n*-butene, one can expect that reaction runs in the pores and not only on the external surface. Some experimental results confirm this idea [7]. The mentioned shape selectivity offers an additional check on the validity of the suggested mechanisms in the pores. A mechanism can be considered to be operating only when the suggested intermediates can be formed *in* the pores. With *n*-butene this means that the intermediates have to fit into the narrow pores of the 10-membered ring zeolites. Various catalytic measurements [6,7,13,14] already indicated that the trimethylpentenes are likely too large to be formed in these materials and molecular modelling has led to the similar conclusion [2]. For example, it has been established [13] that isobutene dimerises very easily to 2,4,4-trimethylpentene on the "open surface" catalyst H_3PO_4/SiO_2. However, the same reaction almost does not proceed with the 10-membered ring molecular sieve SAPO 11 (with a deactivated external surface) although both catalysts contain very similar active sites [6]. Isomerisation of heptane on SAPO 5 and SAPO 11 yields different reaction product patterns [14]. Molecules with a neopentane unit in the structure were not formed in the 10-membered ring molecular sieve.

Even the dimethylhexanes seem to be too large to move freely in the pores. Both above mentioned references [13,14] describe the suppression of formation of the double-branched molecules due to steric constraints in 10-membered ring molecular sieves. Chen et al. [15] claim explicitly that 2,3-dimethylhexane does not fit in the pores of ZSM-5 at room temperatures.

While several catalytic tests have been already performed to show which octenes and octanes can be formed in 10-membered ring zeolites, simple adsorption measurements, testing the inner accessibility of the catalysts for skeletal isomerisation, have not been performed yet. The purpose of this short study is to supply these data.

2. Experimental

Various octenes and octanes were adsorbed on the 10-membered ring borosilicate H-[B]ZSM-5. The template used in the synthesis of this molecular sieve was ethylamine, which ensured an unusually high Si/B ratio equal to 11. The subsequent decomposition in the vacuum at 673 K resulted in the formation of acid form H-[B]ZSM-5 [16]. The structure and crystallinity of this sample was checked using X-ray diffraction, infrared spectra of skeletal vibrations, scanning electron microscopy and sorption capacity measurements. Measurement was performed on spring microbalances in the high-vacuum system. The spring was carefully calibrated before the measurement. About 100 mg of zeolite was used for adsorption, the sample was activated by heating to 673 K (rate 5 K/min) under vacuum and the exact weight of the sample was evaluated after degassing.

Octanes used were 2,4,4-trimethylpentane (Aldrich), 2,4-dimethylhexane (Aldrich) and *n*-octane (Merck). Octenes used were 2,4,4-trimethyl-1-pentene (Aldrich, 99%) and 1-octene (Aldrich, 99%). Hydrocarbons used were carefully cleaned from air and water. They were redistilled under vacuum in situ and dried by a molecular sieve. 2,4-dimethylhexane and 2,2,4-trimethylpentane were carefully cleaned in situ from all impurities that would adsorb faster than the molecules studied. An excess of silicate ZSM-5, capable to adsorb all impurities, was activated in the standard way and after activation it was brought into contact with the octane, for about 30 h. The purity of octanes was checked after adsorption, by using a gas chromatograph (HP 5890, capillary column filled with KCl-treated alumina, FID detector). The following figures were established: 2,4,4-trimethylpentane – 99.8%, 2,4-dimethylhexane – 99.8% and *n*-octane – 99.2%.

Adsorption measurement was performed at 297 K, the temperature of the octane reservoir was 273 K. Temperatures were chosen to keep the ratio $p_0/p_s = 0.2$–0.3 (p_0 = saturation vapour pressure at 273 K, p_s = saturation vapour pressure at the adsorption temperature). The reservoir volume was larger than the relevant volume of microbalances.

3. Results

The acidity of H-[B]ZSM-5 is very low [17] and therefore no isomerisation, polymerisation or cracking of C_8-hydrocarbons was detected with this catalyst. However, adsorption measurement on SAPO 11, H-[Al]ZSM-5 and ferrierite could not be performed because octenes polymerised on the surface of these materials at room temperature. The MFI structure of the borosilicate consists of straight 10-membered 5.2 × 5.7 Å channels interconnected by sinusoidal 5.3 × 5.6 Å channels. The pore diameter is slightly larger than the pore diameters of any catalyst used with success for skeletal isomerisation of *n*-butene (SAPO 11, ZSM-22, ZSM-23 and ferrierite). It means that if any octene does not enter the pores of the borosilicate it certainly does not enter the pores of any 10-membered ring molecular sieve active in skeletal isomerisation of *n*-butene.

Fig. 1 shows the time course of adsorption of 1-octene and of 2,4,4-trimethyl-1-pentene (TMPe). Adsorption of 1-octene is very fast, while almost no TMPe is adsorbed. TMPe does not polymerise and does not block pores of B-ZSM-5 (what happens with more acidic zeolites). When the sample is contacted with TMPe and then TMPe is pumped away, the subsequent adsorption of 1-octene is not influenced. Coadsorption of 1-octene and TMPe (1-octene : TMPe = 1 : 2.3; 1-octene $p_0/p_s = 0.28$, TMPe $p_0/p_s = 0.26$) leads to the same limiting amount adsorbed. Adsorption is slower only because of gas-phase diffusion effects.

Adsorption of *n*-octane is as fast as adsorption of 1-octene (fig. 2). In the limit, about the same amount of both compounds is adsorbed. Diffusion of 2,4-dimethyl-

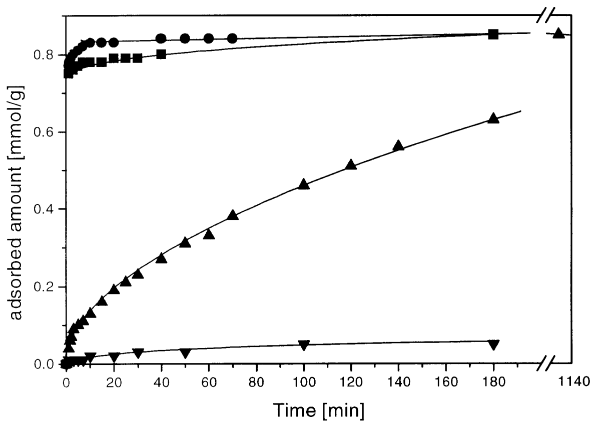

Fig. 1. Adsorption of 1-octene and 2,4,4-trimethylpentene on H-[B]ZSM-5. Standard adsorption conditions. (■) Adsorption of 1-octene, (●) adsorption of 1-octene, TMPe was preadsorbed on the sample and pumped out of system, (▲) mixture of TMPe and 1-octene under standard measurement conditions ($p_{\text{octane}} : p_{\text{TMP}} = 1 : 2.3$), (▼) adsorption of TMPe.

hexane into the pores is much slower than the diffusion of linear molecules. After 45 h of measurement, an equivalent of only 68% of *n*-octane adsorption, is adsorbed. Almost no adsorption was observed when 2,2,4-trimethylpentane (TMPa) was introduced above the borosilicate. This all can be seen in fig. 2.

4. Discussion

Adsorption of *n*-octane and 1-octene is very fast on H-[B]ZSM-5. These molecules enter easily the pores of the 10-membered ring zeolites. The steady state is reached already after 20 min. Adsorption of the double-branched 2,4-dimethylhexane is significantly slower. Even 45 h is not enough to complete the adsorption. 2,4,4-trimethyl-1-pentene and 2,2,4-trimethylpentane probably do not adsorb at all (at 298 K) in the inner space of the molecular sieve. Only a very small amount of these molecules was adsorbed when they were in contact with the 10-membered ring zeolite. This negligible adsorption can be the result of adsorption on the external surface, in the mesopores, or it can be caused by low molecular weight impurities in the adsorbate.

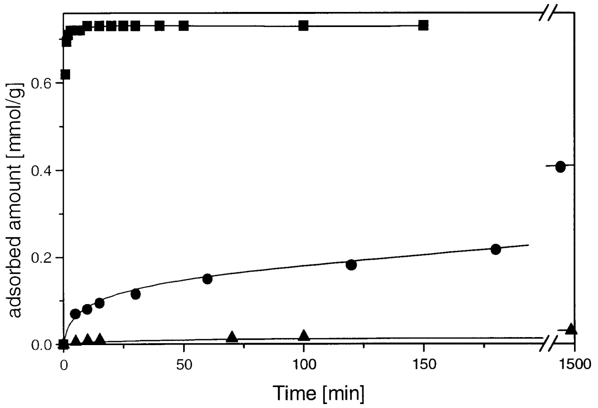

Fig. 2. Adsorption of *n*-octane, 2,4-dimethylhexane and 2,2,4-trimethylpentane on H-[B]ZSM-5. Standard adsorption conditions. (■) *n*-octane, (●) 2,4-dimethylhexane, (▲) 2,2,4-trimethylpentane.

The results are in full agreement with conclusions from the catalytic measurements [13,14]. Obviously, the triple-branched molecules do not fit the channels of the 10-membered ring molecular sieves and cannot be intermediates of any reaction taking place in the pores (i.e. in zeolites without cavities or cross sections). A lower concentration of the double-branched C_8-molecules produced on SAPO 11, compared to SAPO 5 (large pores) and H_3PO_4/SiO_2 (open surface) indicates that the diffusion of the mentioned molecules is slow in small pores [13,14]. This conclusion, is also supported by the data shown above.

Let us now proceed to the conclusions. The reaction runs inside pores, since otherwise the shape selectivity would not play so important a role. From the microporous materials, only the 10-membered ring zeolites and their analogues have been found to be active and selective catalysts for skeletal isomerisation of*n*-butene [10]. When the channels of the zeolites are completely filled by carbonaceous deposits, the catalysts lose their activity [7]. If trimethylpentanes, and of course, a carbenium ion derived from trimethylpentenes, do not fit into the pores of the active materials, they cannot be intermediates of skeletal isomerisation. Similarly, the pseudomonomolecular mechanism on the carbonaceous deposits [4] cannot operate in the pores. It requires formation of a cluster of carbon atoms larger than a neopentane unit operating in the isomerisation mechanism via trimethylpentenes. Thus, if at all, this mechanism can occur only on the outer surface of zeolite grains. However, other results [7,10] show that the isomerisation takes place *in* the pores.

The adsorption results presented above do not completely exclude a mechanism via a 2,4-dimethylhexenium ion. This ion can be formed in the 10-membered ring zeolites. However, the question is whether it can induce a fast reaction. It would be probably trapped in the channels, and it would not move rapidly. In any case, this mechanism, if operating, would not be sufficiently selective. The experiments showed [6,13], that cracking of dimethylhexenes leads to a large amount of by-products. Furthermore, there are some additional arguments against any bimolecular mechanism of*n*-butene isomerisation, in general. If isobutene is to be formed via a molecule of octene, which originates from two molecules of butenes, one would expect that a higher partial pressure would lead to a higher formation of isobutene. However, with a higher partial pressure of *n*-butene, the yield of isobutene decreases because the formation of by-products is faster [13,16]. Further, dimerisation of butenes is not thermodynamically favoured at high temperatures (a higher temperature means a lower extent of dimerisation). However, skeletal isomerisation runs at temperatures higher than 623 K [2,6–9], far above the temperature of an extended dimerisation. Contrary to the expectation based on the idea of a bimolecular mechanism, the selectivity to isobutene significantly increases at about 770 K, when the by-product formation is suppressed obviously by suppression of dimerisation at high temperature [6]. The established role of the kinetic factors (the pressure of butene and the reaction temperature) offers strong arguments against a bimolecular mechanism of the skeletal isomerisation of *n*-butene.

The adsorption test explains the experimentally found shape selectivity of the 10-membered ring zeolites in the skeletal isomerisation of *n*-butene. While the linear or monobranched molecules, like butene and isobutene, can easily move through the channel, diffusion of the double-branched octenes is slow and the triple-branched molecules cannot be formed at all in the channels without cross-sections. Since arguments in the last paragraph indicate that skeletal isomerisation of *n*-butene is a monomolecular conversion, but the by-products (mainly propene and pentenes) are formed by the bimolecular mechanism, catalysts suppressing dimerisation should be more selective. All available information confirms that it is so. However, this study shows also the limits of the shape selectivity. While the by-product formation via trimethylpentenes can be suppressed completely, the formation via dimethylhexenes can only be slowed down. Therefore, it seems not to be possible to design a catalyst which would stop the by-product formation (via dimerisation) completely.

The situation with *n*-butene differs from that of the skeletal isomerisation of *n*-butane to isobutane. 12-membered ring zeolites [11,12], or open surface catalysts like sulfurized zirconia [5], are required for this reaction. This all indicates that dimerisation plays a beneficial role in the isomerisation of *n*-butane.

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