Separation of Branched Hexane Isomers Using Zeolite Molecular Sieves

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A range of small, medium and large pore zeolite, and their modified forms are studied for their ability to separate di- from monobranched isomers of hexane. The separation studies are carried out using high-temperature (250-350°C) gas chromatography. Beta(H,Ba) is found to be the most effective separator of 2,3-dimethylbutane and 3-methyl-pentane and is therefore studied for its sorption capacities toward the two hexane isomers.

Introduction

This work is directed to the improvement of the quality of petrol by separating hydrocarbon mixtures using zeolites. Since maximum hydrocarbon branching is desirable in petrol (hydrocarbons with a branching structure burn more efficiently and thus have a higher "octane rating"), catalytic isomerization is used to isomerize straight-chain hydrocarbons to their mono- or dibranched isomers. To maximize the effectiveness of the isomerization process several preisomerization steps have been designed to separate high-octane hydrocarbons from those of low-octane qualities prior to the isomerization (Gray, 1984; Stem, 1989). This article evaluates zeolites in regard to their ability to selectively adsorb monobranched paraffins but not their dibranched isomers of higher octane rating. Separation of the hexane isomers, 2, 3-dimethylbutane and 3-methylpentane on a series of zeolites was studied as a model system. These two isomers were selected, since their molecular critical diameters are identical (0.56 nm, Choudchary and Akdekar, 1989) which makes the separation very challenging. Beta(H,Ba) proved to be potentially the most effective separator of these two hexane isomers from the industrial point of view and underwent room-temperature liquid-phase adsorption studies, which led to the determination of the pore volume accessible to 2,3-dimethylbutane and 3-methylpentane.

Experimental Studies

The following zeolites were studied in this work: Beta (H,Na), mordenite (Na), silicalite (Na), EU-1 (Na), ZSM-12 (Na), SAPO-5. Some of the above mentioned zeolites were then modified to improve their performance, using boric acid, phosphates and ion exchange modification. Ion exchange enables the zeolite structure to be modified by altering both the electric fields inside the zeolite crystals and adjusting pore size dimensions.

Materials

All tested molecular sieves apart from SAPO-5, which was synthesized in our laboratory (Klimczyk, 1994) were supplied by British Petroleum. The hexane isomers used in the sorption studies (2,3-dimethylbutane and 3-methylpentane) were of high purity (> 99.5%), and were produced by BDH Chemicals Ltd. Helium of high purity, grade 99.995% obtained from BOC Ltd. [Co N4.5(A)], was used as the carrier gas.

Separation studies

The separation properties of the zeolites were investigated using a gas chromatograph (AMS Cambridge Ltd., model 92), fitted with a flame ionisation detector. The GC column was a short glass tube, packed with a pelletized and sieved zeolite (fraction 60-80 mesh). Gas flow rates were measured using a soap bubble manometer. Each newly packed GC column was "conditioned" in the GC by heating at 300°C for an 18-h period with a low flow of the carrier gas (10 $cm^3 \cdot min^{-1}$). This process ensured that preadsorbed low-molecular-weight impurities, which were mainly water and could influence the separation ability of the zeolities, were removed from the column.

Modification of zeolites

Modification of Mordenite (Na) with Boric Acid. 5.0 g of mordenite (powder) was mixed with powdered boric acid (0.15

Table 1. Unit Cell Composition Determined by ICP-AES Analysis*

Abbrev.	Unit Cell Composition	M/Al
mor(Na)	$Na_{8.0}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 1.00
mor(Na,K)	$Na_{0.9}K_{7.1}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.11; K/Al = 0.89
mor(Na,Ba)	$Na_{2.1}Ba_{2.9}AL_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.28; Ba/Al = 0.39
mor(Li,Ba)	$Na_{1.4}Ba_{3.3}Al_{8.0}Si_{38.00}O_{92.0}$	Na/Al = 0.19; Ba/Al = 0.43
mor(Na,Li)	$Na_{5.0}Li_{3.0}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.68; Li/Al = 0.38
mor(Na,Sr)	$Na_{3.6}Sr_{2.7}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.44; Sr/Al = 0.34
mor(Li,Na)	$Li_{1.0}Na_{7.0}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.90; Li/Al = 0.19
mor(Li,K)	$Li_{1.9}K_{6.0}Al_{8.0}Si_{38.0}O_{92.0}$	K/Al = 0.94; Li/Al = 0.26
beta(H,Ba)	$H_{3.0}Ba_{4.0}Al_{11.0}Si_{97.0}O_{217.0}$	Ba/Al = 0.38

*Si/Al ratios are 5.2 and 8.0 for mordenite and beta zeolites, respectively. 1.2% maximum error determined from standard deviation of the ICP-AES readings, which was 0.01 (concentration of each element in a given solution was read 10 times before the average value was determined), accuracy of the sample weighting 0.001 g and the accuracy of the volume measurements 0.25 cm^3.

g), and then 3 cm^3 of water was added. The mixture was stirred for a few minutes at room temperature, and after that the sample was thermally treated for 1 h at 110°C and for another 15 min at 400°C, both in air.

Modification of Silicalite with $NH_4H_2PO_4$. 1.5 g of silicalite (powder) was placed in 40 cm^3 of 1-mol·dm^{-3} $NH_4H_2PO_4$ solution, and then the mixture was heated at 70°C until the water evaporated.

Modification of SAPO-5 with K_3PO_4. 5.0 g of SAPO-5 (powder) was mixed with 0.5 g of dry K_3PO_4, and then 2 cm^3 of water was added. The mixture was then heated at 110°C for 1 h in air.

Modification by Ion Exchange. The following zeolites were modified by ion exchange: mordenite, beta, EU-1, and ZSM-12. All modifications were performed on the pelletized zeolites (fraction 60-80 mesh) (Klimczyk, 1994).

Chemical analysis by ICP-AES

The chemical composition of both modified and unmodified zeolites was determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The zeolites to be analyzed were brought into solution by fusion. Two fluxes were used: $LiBO_2$ and, for the determination of Li, Na_2CO_3. The instrumental system used in this study was the Perkin Elmer Plasma 40 type ICP-AES linked to an IBM-PC. Table 1 shows the unit cell compositions of some of the modified zeolites, determined from the ICP-AES analysis. ^{27}Al and ^{29}Si MAS-NMR spectroscopy was used to check whether aluminium had been removed from the mordenite and beta frameworks in the process of the ion exchange modifications, and this information, together with the absence of peaks at 0 ppm due to octahedral aluminium in the obtained spectra, showed that aluminium atoms had not been removed from the framework.

Sorption capacities

The most effective separator, beta(H,Ba) zeolite, was investigated with regard to its sorption capacity for 2,3-dimethylbutane and 3-methylpentane at room temperature. 1,3,5-triisopropylbenzene (97%, Aldrich) was used as a nonadsorbed solvent. The adsorption studies were performed using the Perkin Elmer gas chromatograph, which detected changes in the concentration of the individual hexane isomers in contact with the zeolites. Analysis was performed using a gas chromatography column (162 cm × 0.4 cm) packed with 3% OV-101 on 80-100 chromosorb W-HP (Alltech Associates, Inc.) operated at 200°C with helium as a carrier gas (25 cm^3·min^{-1}). A zeolite sample (about 1.2 g) was dehydrated in a tube furnace (Carbolite Furnaces) under vacuum at 300°C for 5 h. After cooling to 25°C, 5 cm^3 of a solution of the hexane isomer in 1,3,5-triisopropylbenzene (6.0% v/v) was injected directly into the cell containing the zeolite. During the experiment, the cell was periodically shaken and the composition of the liquid mixture was measured at 10–20-min intervals until adsorption equilibrium was obtained.

Results and Discussion

The retention times of pure 2,3-dimethylbutane and 3-methylpentane on the modified and unmodified molecular sieves are presented in Table 2. The zeolites not included in this table are either unmodified zeolites that did not retain the two hexane isomers (the retention times of both 2,3-dimethylbutane and 3-methylpentane were close to zero) or modified forms that did not show any improvement over the unmodified version as far as their sorption properties are concerned.

EU-1, silicalite, and ZSM-12 were expected to adsorb 3-methylpentane but not 2,3-dimethylbutane, which theoretically is too large to enter the zeolite's pores. Surprisingly they proved to be able to retain 2,3-dimethylbutane as well as 3-methylpentane, although their retention times were relatively short (Table 2). Sorption of 2,3-dimethylbutane might be explained by the vibrational flexing of the zeolite framework atoms at these high temperatures, resulting in an effective enlargement of the pore size. A more probable explanation is that they were retained by interactions with the surface of the zeolite. This would explain the short retention time compared to larger pore zeolite. Mordenite and SAPO-5, on the other hand, proved to have a high affinity for both 2,3-dimethylbutane and 3-methylpentane, as they retained the hexane isomers for a relatively long time (Table 2). This was expected as the pores of these particular molecular sieves are larger than the molecular dimensions of the hexane isomers. The modifications of mordenite with boric acid together with the phosphate modifications performed on SAPO-5 and silicalite proved to be extremely unsuccessful as they led to a narrowing of the pores of these materials to such an extent that the retention times of both hexane isomers become close to zero.

The results of the experiment show that the sorption properties of a zeolite depend strongly on the zeolite pore size and shape. For example, EU-1 zeolite proved to sorb both hexane isomers, while SAPO-11, having a cross-sectional area about twice that of EU-1, was unable to sorb even the monobranched hexane isomer. This was due to the fact that EU-1 has more circular pores compared to the elongated pores of SAPO-11, and the hexane isomers could force themselves through the channel openings of EU-1 by compression (Choudchary and Akolekar, 1989). They also show that the sorption properties of a zeolite are markedly affected by both the size and charge density of the cations present in the zeolite channels. It creates a characteristic environment for an

Table 2. Retention Times of Pure 2, 3-Dimethylbutane ($t_{R\ 2,3-}$) and 3-Methylpentane ($t_{R\ 3-}$) on a Variety of Zeolites*

Zeolite	Temp. °C	$t_{R\ 2,3-}$ min	$t_{R\ 3-}$ min	$t_{R3-} - t_{R2,3-}$ min
Mordenite (Na)	300	5.41	6.35	0.94
	325	4.24	4.65	0.41
Mordenite (Na,Li)	325	5.19	6.11	0.92
	340	3.75	4.19	0.44
	350	2.88	3.06	0.18
Mordenite (Na,K)	300	4.13	5.92	1.79
	325	2.33	3.34	1.01
	350	1.37	1.86	0.49
Mordenite (Na,Ba)$_a$	300	8.47	11.04	2.57
	325	4.59	6.55	1.96
	350	2.68	3.17	0.49
Mordenite (Na,Ba)$_b$	325	8.03	11.42	3.45
	340	5.50	7.89	2.39
	350	4.16	6.34	2.18
Mordenite (Li,K)	300	3.67	5.54	1.87
	325	2.04	3.33	1.29
	350	1.49	2.20	0.71
Mordenite (Li,Na)	300	8.23	9.80	1.57
	325	4.32	5.00	0.68
	350	2.76	3.37	0.61
ZSM-12 (Na)	250	2.59	3.97	1.38
	300	0.85	1.49	0.64
	325	0.33	0.53	0.20
Silicalite (Na)	250	2.87	5.09	2:22
	300	0.97	1.73	0.76
	325	0.37	0.57	0.20
EU-1 (Na)	300	0.97	1.45	0.48
	325	0.30	0.49	0.19
SAPO-5	300	6.00	6.68	0.68
	325	4.55	5.00	0.45
Beta(H,Ba)	300	8.66	11.42	2.76
	325	4.41	6.17	1.76
	350	2.56	3.30	0.74

*Gas flow rate: 30.0 $cm^3 \cdot min^{-1}$. Retention times of the hexane isomers on each zeolite were measured three times. Standard deviation of a given retention time was 0.025 min.

adsorbed molecule and its interactions with the zeolite framework. As an example, the introduction of Li^+ into mordenite (Na) led to a significant increase in the retention times of both 2,3-dimethylbutane and 3-methylpentane (Table 2), which was probably caused by the high charge density of this particular cation, in comparison to that of Na^+ ion (the charge density of Li^+ cation is 2.21 e nm^{-3}, whereas that of Na^+ cations is 0.56 e nm^{-3}). The high charge density of Li^+ has probably enhanced an electrostatic-type interaction between the absorbed molecules and the oxygen ions of the zeolite framework. The influence of the size of the cation on the sorption properties of zeolites can be exemplified by the performance of mordenite (Na,Ba)$_a$, which retained the hexane isomers for a longer period of time than mordenite (Na) (at 300°C 2,3-dimethylbutane left the GC column packed with mordenite (Na,Ba)$_a$ after 8.47 minutes while at the same temperature mordenite (Na) retained 2,3-dimethylbutane for 5.41 minutes). The charge densities of Na^+ and Ba^{2+} are comparable; however, the diameter of Ba^{+2} cations is larger than that of Na^+ (2.7 nm and 1.9 nm respectively, Ball and Norbury, 1974). This suggests that in this particular case the size of the cation seems to be more crucial than its charge density. The larger the cations in the zeolite channels, the smaller the distance between the adsorbed molecules and the walls of the zeolite channels and hence the stronger the molecular-type interactions between the adsorbed molecule and the zeolite.

Some of the zeolites studied—ZSM-12 (Na), silicalite (Na), mordenite (Na,Ba)$_a$, mordenite (Na,Ba)$_b$, mordenite (Na,K) and beta(H,Ba)—underwent further studies with regard to their ability to separate mixtures of hexane isomers. The mixture of hexane isomers contained 0.5×10^{-4} cm^3 of each of the following hexane isomers: 2,3-dimethylbutane, 3-methylpentane, 2-methylpentane and *n*-hexane, except for the mixtures separated on mordenite (Na,Ba), mordenite (Na,Ba)$_a$ and beta(H,Ba), where the mixture contained 0.5×10^{-4} cm^3 of 2,3-dimethylbutane, 0.5×10^{-4} cm^3 of 3-methylpentane, 0.1×10^{-4} cm^3 of 2-methylpentane and 0.1×10^{-4} cm^3 of *n*-hexane. The resolution factors (k) of 2,3-dimethylbutane and 3-methylpentane on the zeolites studied are presented in Table 3 and were calculated using the following equation:

$$k = 2d/w_1 + w_2$$

where d is the distance between peak 1 and 2, respectively, and w_1, w_2 are the widths of the two peaks measured at their base.

Most unexpectedly, mordenite (Na,Ba)$_a$ and mordenite (Na,Ba)$_b$ were unable to separate the hexane isomers in the mixture producing overlapping peaks, whereas beta(H,Ba) proved to be very effective at separating 2,3-dimethylbutane from 3-methylpentane with a resolution of 3.2 and a difference of 1.96 min in the retention times of 2,3-dimethylbutane and 3-methylpentane at 325°C. Although the resolution of 2,3-dimethylbutane and 3-methylpentane for ZSM-12 (Na) is reasonably large at 300°C (Table 3), the difference in the retention times of these two hexane isomers is significantly smaller (0.64 min); hence, this particular zeolite would be less useful for industrial separation.

The molecular sieves adsorbing both hexane isomers always retained 3-methypentane for a longer period of time than they did 2,3-dimethylbutane. The reason is that, although these two hexane isomers are of very similar size and hence the penetration of the zeolite pore system is similar, the interactions between the individual isomers and the atoms of the zeolite framework or cations present in the zeolite channels are different (the adsorption of 3-methylpentane is stronger than that of the more spherical 2,3-dimethylbutane) (Klimczyk, 1994). This in turn leads to differences in their diffusion rates through the zeolite pores, which was confirmed by the diffusion studies carried out on the most successful separator, beta(H,Ba). The diffusion coefficients of the

Table 3. Resolution Factors (k) of 2,3-Dimethylbutane and 3-Methylpentane on Various Zeolites*

Zeolite	Temp. °C	k	$(t_{R3-} - t_{R2,3-})_{mix}$ min
mordenite (Na,K)	325	0.8	1.01
ZSM-12	300	1.8	0.64
	350	1.0	0.20
beta(H,Ba)	325	3.2	1.96

*Gas flow rate 30.0 $cm^3 \cdot min^{-1}$. Separation factors of 2,3-dimethylbutane and 3-methylpentane on mordenite (Na,Ba)$_a$, mordenite (Na,Ba)$_b$ and silicalite were not determined due to the overlapping of the corresponding chromatographic peaks.

pure hexane isomers were measured using the gas chromatograhic technique (Klimczyk, 1994). Analysis of the shape of the chromatographic peaks at different temperatures, and flow rates for each individual isomer proved that, although the diffusivities of both 2,3-dimethylbutane and 3-methylpentane are of the same order of magnitude, the diffusion coefficient of 2,3-dimethylbutane appears to be slightly larger than that of 3-methylpentane (Klimczyk, 1994). At 325°C the diffusion coefficient of 2,3-dimethylbutane was found to be $3.00\times 10^{-6}\ \mathrm{cm^2\cdot s^{-1}}$, whereas the diffusion coefficient of 3-methylpentane was found to be $2.70\times 10^{-6}\ \mathrm{cm^2\cdot s^{-1}}$ (Klimcyzk, 1994).

The adsorption capacities of beta(H,Ba), for 2,3-dimethylbutane and 3-methylpentane are $0.099\ \mathrm{gg^{-1}}$ and $0.104\ \mathrm{g^{-1}}$, respectively. Although in each case the adsorbed amounts of the individual hexane isomers were comparable, the amount adsorbed of 2,3-dimethylbutane was less than that of 3-methylpentane. This indicates that parts of the zeolite are less accessible to the more branched 2,3-dimethylbutane, and hence the packing of this dibranched hexane isomer is less efficient.

Conclusions

Until recently, only one zeolite (ferrierite) has been suggested as being able to maximize the effectiveness (separation of dibranched product) of the isomerization of normal and monobranched paraffins to dibranched paraffins of higher octane number (Stem, 1989). Beta(H,Ba) of this work has been shown to be very successful for these separations; since their pore sizes are larger than those of ferrierite, they are applicable to the separation of a broader range of hydrocarbons. The separation of 2,3-dimethylbutane from its monobranched isomers and *n*-hexane appears to be very good, considering that in this particular work a small sample of the zeolite (about 1.0 g) was studied in short column, whereas in industry the length of the zeolite bed would be significantly larger, resulting in greater separation. Further work is under way to investigate the abilities of other ion-exchanged beta zeolites in the separation of dibranched from monobranched hexane isomers.

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