Molecular Sieving of n-Butenes by Microporous Silicoaluminophosphates

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Of all three n-butenes (but-1-ene, cis-but-2-ene and trans-but-2-ene) only the trans-isomer can easily access the pore system of the molecular sieve SAPO-17 resulting in appreciable adsorption and allowing a promising adsorptive separation of stereoisomeric butenes at temperatures of 330–395 K, where catalytic reactions do not occur.

Stereoisomers of C_4–C_6 olefins are normally separated by azeotropic distillation using ethers and ketones. The azeotropic mixture is formed with the cis-isomers which have the highest boiling points. Extraction using carbamides is also possible. Adsorption methods utilize zeolites CaA and cation exchanged X and Y zeolites. Separation of but-1-ene from the cis- and trans-but-2-enes is reported to be possible over KX and KBaX (17.8% K_2O),[1] with adsorption at 323 K and atmospheric pressure. The drawback of adsorption methods using higher temperatures is the undesired onset of reactive transformations of butenes leading to catalytic isomerization, dimerization or oligomerization.

Separation of stereoisomeric cis- and trans-but-2-enes through adsorption processes has not been reported so far.

We have found that the silicoaluminophosphate structure SAPO-17 is able to adsorb trans-but-2-ene in large excess at low temperatures compared with but-1-ene and cis-but-2-ene. This offers the possibility of separating trans-but-2-ene from the cis-isomer (and from but-1-ene) by an adsorption procedure using a molecular sieve adsorbent. SAPO-17 is isostructural with the known zeolite erionite and has an 8-ring channel system with elliptical pore apertures 0.36×0.51 nm in size. Its synthesis and acidic properties are described elsewhere.[2,3] The sample used had a solid composition of 43 Al_2O_3, 54 P_2O_5 and 3 SiO_2 determined by chemical analysis. Characterization data, specifically ammonia desorption experiments, proved the isomorphous substitution of Si^{IV} in lattice positions, replacing most probably P^V. An overall acidity of about 0.5 mmol g^{-1} can be detected which is in fair agreement with the molar silicon content.

Adsorbed amounts of n-butenes at fixed butene concentration (5% v/v) and temperatures of 333, 373 and 393 K were determined from breakthrough curves observed after a step change from pure hydrogen, flow rate 1 $cm^3 s^{-1}$, to a hydrogen stream containing 5% of the respective butene at a constant flow rate. A reverse step change allowed desorbed amounts to be determined. Before each measurement and between the adsorption–desorption cycles the catalyst pellets (consisting of 65% molecular sieve and 35% SiO_2 binder in the form of cylinders with diameters of 2 mm) were annealed in situ at 600 K under a flow of hydrogen for 0.5 h to remove adsorbed water from the fresh catalysts and irreversibly adsorbed butene from the samples following isothermal desorption. The percentage of butenes adsorbed on the binder material has been investigated separately and the amounts have been subtracted from the adsorbed amounts on the catalyst pellets taking into account temperature, kind of butene, concentration of butenes and percentage of binder. Catalytic double bond isomerization is observed to start at about 425 K. A detailed description of methods and results will be given elsewhere.[4] For comparison the silicon-free aluminophosphate structure $AlPO_4$-17 was included.

Results are shown in Fig. 1. Fig. 1(a–c) demonstrates the dependence of adsorbed amounts of the respective n-butene on temperature as observed over $AlPO_4$-17 as well as SAPO-17. Fig. 1(d–f) shows the corresponding results for that part of the butenes which could be desorbed under isothermal conditions. It turns out that $AlPO_4$-17 has nearly the same adsorption capacity (at 333 K) for all three n-butenes, ca. 1 mmol g^{-1}. The overall amounts of adsorbed butenes decrease with increasing temperatures but more markedly for trans-

but-2-ene than for the other isomers. SAPO-17 exhibits a clearly different behaviour towards but-1-ene and cis-but-2-ene. In contrast to $AlPO_4$-17, the adsorption capacity for but-1-ene and cis-but-2-ene is very low and the amounts adsorbed increase with increasing temperatures. Adsorption of the trans-isomer, however, is virtually unchanged. Consequently, the adsorbed amount of trans-but-2-ene exceeds that of the other isomers by a factor of ca. 7 at 333 K.

After isothermal desorption at 333 K, ca. 50% of but-1-ene and cis-but-2-ene, but only ca. 25% of trans-but-2-ene remain irreversibly on the adsorbents. In the case of $AlPO_4$-17 the percentage of irreversibly adsorbed butenes strongly decreases at higher temperatures and approaches zero at about 393 K, whereas the amounts of irreversibly adsorbed but-1-ene and cis-but-2-ene in case of SAPO-17 remain almost constant at the temperatures of the experiments.

It is obvious that the access to the pore system of SAPO-17 is restricted to a great extent for but-1-ene and cis-but-2-ene but not for trans-but-2-ene. Comparison with properties of the non-substituted $AlPO_4$-17, where such differentiation is not observed, illustrates that SAPO-17 has acquired this ability
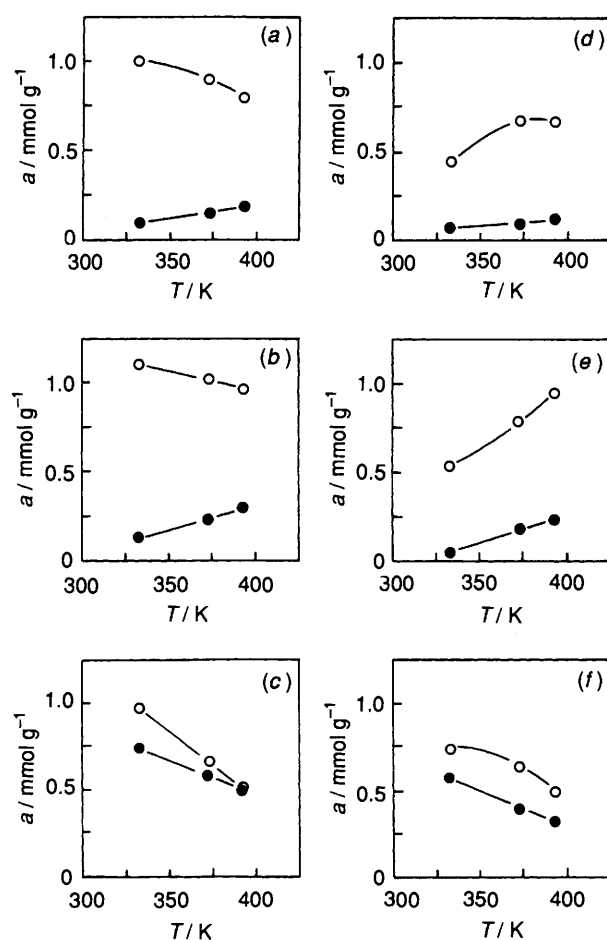

Fig. 1 Adsorbed (a–c) and desorbed (d–f) amounts of n-butenes (a, d but-1-ene, b, e cis-but-2-ene, c, f trans-but-2-ene) over $AlPO_4$-17 (○) and SAPO-17 (●) vs. temperature

through the presence of silicon and hence through the modification of lattice properties associated with the emergence of Brønsted acid sites.

Most probably, the discrimination of n-butenes by SAPO-17 results from a differentiated electrostatic interaction between the negatively charged anion lattice and the n-butenes that differ in their polarity. $trans$-But-2-ene, because of its symmetry, has no permanent dipole moment, whereas cis-but-2-ene has a moment directed perpendicular to its double bond. But-1-ene also possesses a permanent dipole moment, but its structure is more flexible, since free rotation around the central C–C axis allows at least six different conformations.[5]

Obviously, the orientation of but-1-ene and cis-but-2-ene dipoles towards the electrostatic field at the pore entrance is unfavourable for entering the pores and adsorption is mainly confined to the exterior of the molecular sieve crystals. In contrast, $trans$-but-2-ene can access the pore system easily. Therefore, the overall adsorption capacity for $trans$-but-2-ene is only marginally affected through the presence of Brønsted sites, although more $trans$-but-2-ene is fixed irreversibly ($ca.$ 0.1 mmol g^{-1}) on SAPO-17 at 373 and 393 K. This points to an interaction of $trans$-but-2-ene with Brønsted sites, where the butene is probably hydrogen bonded via protons of the acid sites. In case of but-1-ene and cis-but-2-ene an activation energy is probably necessary for the diffusion of the isomers into the pore system.

Adsorption experiments using the molecular sieve SAPO-11, which has non-intersecting pores of 0.39 × 0.63 nm size, show a uniform behaviour of all three n-butenes. This points to the paramount importance of the pore apertures, besides the electronegativity. Both a suitable pore size and the presence of an electric field at the pore entrance combines in this unique discrimination between the n-butene isomers.

Therefore, a separation of $trans$-but-2-ene from cis-but-2-ene seems to be possible by means of adsorption–desorption cycles under convenient conditions using the unique properties of the molecular sieve SAPO-17. Experiments to elucidate the adsorptive properties of the parent erionite are in progress. It is expected that the effect described here can be exploited on a larger scale. Optimum conditions have still to be found.

References

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