Liquid phase separation of 1-butene from 2-butenes on all-silica zeolite RUB-41

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Received (in Cambridge, UK) 18th December 2007, Accepted 29th February 2008
First published as an Advance Article on the web 28th March 2008
DOI: 10.1039/b719463c

The all-silica zeolite RUB-41, containing 8- and 10-membered rings, is able to separate *trans*-2-butene and *cis*-2-butene from 1-butene and represents a possible improvement in isolating pure 1-butene from a butene mixture.

The separation of mixed C_4-alkenes and butadiene is a highly energy-intensive process in the chemical industry due to the close boiling points of the unsaturated C_4 isomers. Several separation methods can be combined to maximize the feedstock utilisation.[1] Butadiene is mostly removed by extractive distillation. Next, isobutene can be removed under mild acid catalysis to selectively form methyl *tert*-butyl ether or *t*BuOH. The most critical step is to separate 1-butene from 2-butenes, as high-purity 1-butene is needed in the production of *e.g.* linear low density polyethylene (LLDPE). Further separation of the 2-butenes is not of interest as these molecules react analogously in further processing by dehydrogenation, oligomerisation or alkylation. For the fractionation of 1-butene from the 2-butenes, high multi-plate low-temperature columns are currently used, and there is a clear need to propose alternative processes based on selective adsorption. Patent literature has already reported on the possible separation of 1-butene out of a mixed C_4 stream by utilizing cation exchanged X zeolites.[2] On a K-exchanged X zeolite, 1-butene is preferred over *trans*-2-butene, an effect ascribed to favorable enthalpic interaction between the exchanged cation and the π cloud of the olefin. The reverse order is observed when the separation is based on a true shape selective effect. Thus, 8-membered ring zeolites like NaCaA (LTA),[3] erionite or AlPO-17 (ERI),[4] and recently all-silica DD3R (DDR),[5,6] all-silica chabazite (CHA),[7] or ITQ-32 (IHW)[8] all prefer *trans*-2-butene over 1-butene, simultaneously excluding *cis*-2-butene from the lattice. This order is consistent with the critical diameters of the isomers: *trans*-2-butene (0.431 nm) < 1-butene (0.446 nm) < *cis*-2-butene (0.494 nm).[5] However, the application of such zeolites has exclusively been demonstrated in the gas phase,[3–8] while liquid phase operation offers the advantage of maximised bed utilisation, as indicated by a vast body of patented technology.[9,10] Here we report on the butene sorption properties of all-silica RUB-41 zeolite. Remarkably, this zeolite prefers both *trans*- and *cis*-2-butene over 1-butene. Moreover, column breakthrough experiments prove that efficient separations can be performed in the liquid phase.

Zeolite RUB-41 (RRO topology) was prepared in a two-step synthesis *via* a layered precursor.[11] First, hydrothermal synthesis at 150 °C in the presence of dimethyldipropylammonium hydroxide resulted in the layered precursor RUB-39. Controlled calcination of this precursor at 520–560 °C resulted in topotactic condensation of the Si–OH groups to form a 3-dimensional framework. It comprises a 2-dimensional intersectional pore system consisting of an 8-membered ring channel (0.27 × 0.5 nm) along [001], and a 10-membered ring channel (0.4 × 0.65 nm) along [100]. The crystals used in this work were flat and polygonal, with a thickness well below 1 μm, and with the dimensions of the (010) faces between 2 and 6 μm. The XRD patterns showed excellent agreement with those previously reported.[11] By volumetric physisorption measurements it was established that the pore volume accessible to N_2 molecules at 77 K amounted to 0.18 mL g^{-1}. The calcined samples were stored at room temperature, and shortly dried at 200 °C before use.

First, equilibrium isotherms were measured for uptake of the single butene isomers in RUB-41 from cyclohexane solutions. The latter were prepared by contacting the butenes at various pressures with the solvent in a Parr pressure vessel. After addition of the butene solution to dry RUB-41 and equilibration for various times up to 24 h, the liquid supernatant was directly injected in a GC.†

Sorption isotherms at 293 K are shown in Fig. 1. *Trans*-2-butene and *cis*-2-butene are much more strongly adsorbed than 1-butene or isobutene. For the latter, a plateau in the isotherm is not even reached at solution concentrations of 1 M. Especially at low concentrations, there is already a strong uptake of *trans*- or *cis*-2-butene. The maximum intraporous concentrations amount to 6.6 M for *trans*- and 5.0 M for *cis*-2-butene, corresponding to 0.095 mL liquid (*trans*) or 0.077 mL (*cis*) per g of zeolite. This convincingly proves that sorption must take place inside the pores. Note that the absorbed volumes are somewhat smaller than the pore volume accessible to N_2. This could be due to small defects hindering pore access; on the other hand, the small N_2 molecules can probably be packed more efficiently inside the pores than the rather rigid 2-butene isomers.

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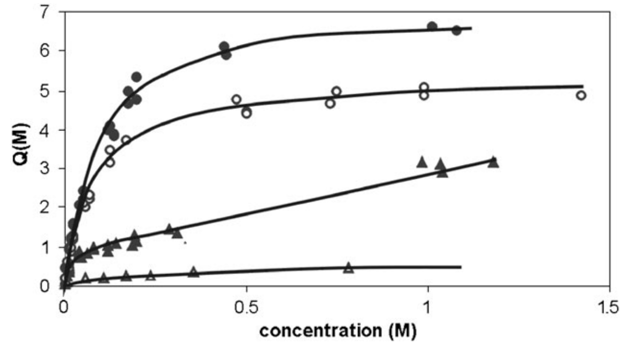

Fig. 1 Adsorption isotherms at 293 K after 24 h: *trans*-2-butene (●), *cis*-2-butene (○), 1-butene (▲), isobutene (△). *Q*(M) is the molar concentration of butene in the pore system.

Next, competitive adsorption experiments were performed using mixtures of butenes with a total concentration of 0.275 M in cyclohexane. The experiments were done in batches at 293 K and uptake was measured after 24 h.

Fig. 2 shows that there is only a weak selectivity between *trans*-2-butene and *cis*-2-butene. When RUB-41 is exposed to mixtures of *trans*-2-butene–isobutene and *cis*-2-butene–isobutene, there is a clear size-exclusion of the branched isomer, as expected for zeolites with 10-membered ring or smaller pores.[10,12] In the case of an equimolar mixture of *cis*-2-butene–1-butene or *trans*-2-butene–1-butene, both 2-alkenes are preferentially adsorbed. This trend *trans*- ~ *cis*- > 1-, as observed for RUB-41, is at contrast with the usual observations with 8-membered ring zeolites, *viz. trans*- > 1- ~ *cis*-. In the latter case, the order is the same as that of the critical diameters of the isomers (*cf. supra*). Thus, zeolites with close-to-circular 8-membered ring pores between relatively large cages, such as those with LTA, CHA, ERI, DDR or IHW topologies, separate butenes by kinetic, shape-selective effects. However, for RUB-41, the equilibrium data of Fig. 1 and 2 show that the separation of 2-butenes from 1-butene is not due to different diffusion coefficients, as the isotherms were recorded after sufficiently long times. The preference of RUB-41 for 2-butenes over 1-butene must be due to thermodynamic rather than kinetic effects. Possible explanations are that the 2-butenes are more efficiently packed inside the pores than 1-butene; or 1-butene might lose more of its conformational entropy when it becomes confined to the RUB-41 pores. In this respect it must be remarked that the pore architecture of RUB-41 is quite different from that of the aforementioned 8-MR zeolites: firstly, the RUB-41 interior is an interlayer gallery rather than a collection of cages, and secondly, the largest pores are distorted elliptical 10-membered ring pores rather than circular 8-membered ring pores.

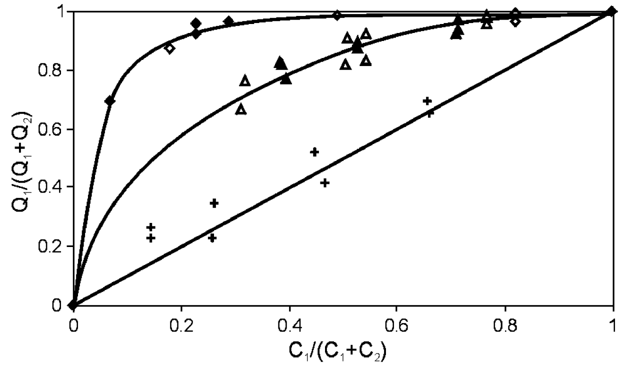

Fig. 2 Competitive adsorption of butene mixtures at 293 K after 24 h. Ratios of intraporous concentrations Q_1(M)/(Q_1(M) + Q_2(M)) *vs.* solute concentration C_1(M)/(C_2(M) + C_1(M)). Olefins 1 and 2 are, respectively, *trans*-2-butene–isobutene (◆), *cis*-2-butene–isobutene (◇), *cis*-2-butene–1-butene (▲), *trans*-2-butene–1-butene (△), *trans*-2-butene–*cis*-2-butene (+).

As *cis*-2-butene is generally accepted to be sterically excluded from 8-membered ring pores, it is of interest to know its diffusion coefficient for uptake *via* the 10-membered ring pores of RUB-41. Kinetic uptake experiments were performed for the *trans* and *cis* isomers (Fig. 3).

As there is a pronounced difference between *trans*- and *cis*-2-butene uptake profiles, internal diffusion seems to control the uptake rate. Hence resistance in a surface film can be neglected, which is also evidenced by the lack of a time lag in the uptake curves. The data points were fitted with the appropriate equation for unidirectional diffusion into a slab ($l = 2 \times 10^{-6}$ m):‡[13]

$$\frac{C_t}{C_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{\exp(-(2n+1)^2\pi^2 Dt/4l^2)}{(2n+1)^2}$$

From the data, a diffusion coefficient for *trans*-2-butene was estimated at 2.4×10^{-14} m^2 s^{-1}, against 8×10^{-15} m^2 s^{-1} for *cis*-2-butene. This order is expected in view of the critical diameters.[5] While slow uptake kinetics could be a problem in designing a large throughput process, the diffusion coefficient of the *cis*-isomer is only three times smaller than that of the *trans*-isomer; other parameters such as crystal size could be optimized when designing a process.

In order to prove the potential of RUB-41 for practical separation, a 7.5 cm column was filled with 0.92 g all-silica RUB-41, and binary mixtures of butenes in cyclohexane were pumped through. 1-Butene appears at the column outlet well before either *trans*-2-butene or *cis*-2-butene (Fig. 4). Upon breakthrough of 1-butene, its outlet concentration is temporarily even higher than the feed concentration. This 'roll-up' effect indicates that some 1-butene which initially might have been intruding into the pores, is eventually displaced by the

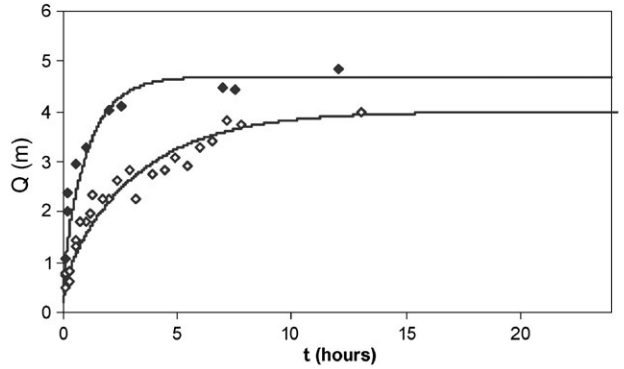

Fig. 3 Time-dependent uptake of *cis*-2-butene (0.206 M, ◇) and *trans*-2-butene (0.171 M, ◆) at 293 K. The data points were fitted with the Craig equation for diffusion into a slab.

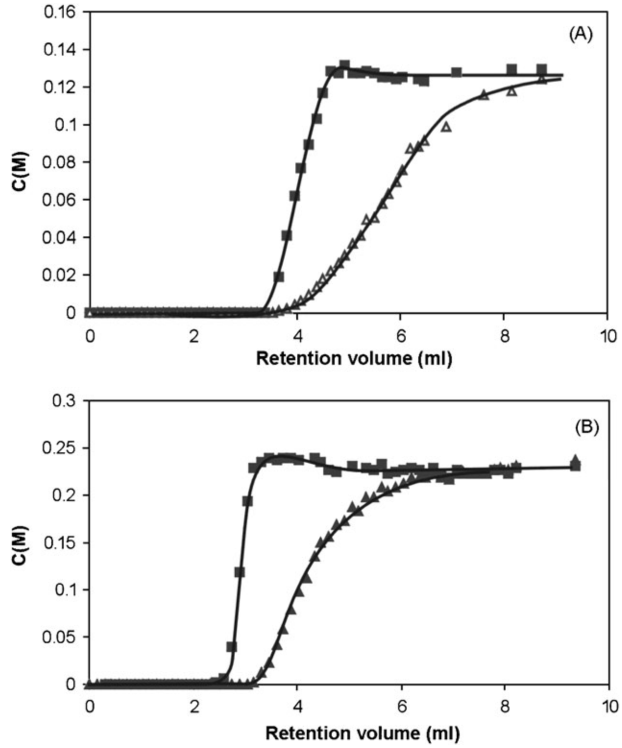

Fig. 4 Breakthrough experiments with binary butene solutions in cyclohexane on a 7.5 cm column filled with RUB-41 at 298 K: effluent concentrations, *C*(M), of (A) *cis*-2-butene (△)–1-butene (■) and (B) *trans*-2-butene (▲)–1-butene (■) as a function of eluted volume. Column inner diameter = 4.2 mm.

2-butene isomer. These breakthrough curves prove that the preference of RUB-41 for 2-butenes is sufficiently high over a broad concentration range to allow practical separations.

Summarizing, we have revealed that RUB-41 is capable of liquid phase separation of 2-butenes from 1-butene. As such, technology based on this zeolite is an attractive option compared to *e.g.* the consecutive use of 2 zeolite types, such as siliceous chabazite and AlPO-34, for the two-step isolation of *trans*-2-butene and 1-butene from a linear butene feedstock.[7] The unique properties of this zeolite are likely a consequence of its particular pore architecture.

We are grateful to BASF AG for support in the INCOE framework.

Notes and references

† As butenes are highly volatile, evaporation of butenes was consistently avoided by eliminating any headspace above the liquid phase. Thus, vials for batch sorption experiments or for chromatographic analysis were completely filled with liquid. Butene analysis was performed with a Shimadzu 2014 GC and CP-SIL-5CB column at 30 °C.

‡ If diffusion of butenes through the distorted 8-MR pores is neglected, the uptake can be considered as unidirectional, starting at the (100) face along the 10-MR pores. The depth of the slab (*l*) corresponds to half the average crystal width along the *a*-direction, or 2 μm.

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