Pure silica ITQ-32 zeolite allows separation of linear olefins from paraffins†

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ITQ-32 is able to separate propene from propane and represents a clear improvement with respect to previous zeolites in achieving the separation of *trans*-2-butene and 1-butene from the C_4 fraction using only one zeolite.

Energy saving and economic reasons have directed companies to look for separation technologies that improve the energy balance, raw materials and cost effectiveness. In this regard, olefin–paraffin separations are of particular interest, since the separation of light olefins (ethene, propene and butenes) from light paraffins (ethane, propane and butanes) is currently performed by cryogenic distillation, which is a highly energy demanding process.[1] Therefore, adsorption processes that are able to discriminate between olefins and paraffins are of great interest in this area and have been investigated in recent years.[2] Besides the interest in the synthesis of ultralarge pore zeolites for catalysis, electronics and drug delivery,[3–6] a number of zeolites with small pores have been reported for olefin–paraffin separations, including Cu- and/or Ag-exchanged zeolites[7] and neutral all-silica[8–11] or aluminophosphate molecular sieves.[12,13] Cu- and Ag-exchanged materials accomplish the gas separation process through cation–olefin π-complexation interaction,[14] while in the case of neutral zeolites and aluminophosphates the separation is based on a molecular sieve effect,[15] which presents clear benefits in terms of stability and long term operation with respect to cation-exchanged zeolites. Importantly, zeolitic materials are able to discriminate between paraffins and olefins based on kinetic as well as on steric effects.[16] It is clear that, for performing olefin–paraffin separations, the most preferred zeolites will be those having the lowest acidity to avoid olefin oligomerisation that will lead to pore blocking after prolonged time on stream.[10,11] In this regard, the pure silica zeolites are more desirable than uncharged aluminophosphates as the former possess a lower concentration of defects.

The advent of ITQ-32 zeolite (IHW), a new microporous material with small pore apertures, may open more possibilities for light hydrocarbons separation.[17] Its framework topology is described as a bidirectional structure formed by 8-membered ring (8MR) pores with apertures of 3.5 × 4.3 Å connected by 12MR channels that generate large cages, leading to a material with relatively large micropore volume (0.17 $cm^3 g^{-1}$) which can also be prepared as purely siliceous. In this work, we will show that the use of pure silica ITQ-32 zeolite makes it possible to perform olefin and paraffin separations. Specifically, we show here the potential use of ITQ-32 in the propene–propane and butenes–butane separations by means of thermodynamic and kinetic studies of gas adsorption at different temperatures using gravimetric measurements.

Pure silica ITQ-32 was synthesised following the procedure previously described.[17] Prior to the adsorption experiments, the zeolite was submitted to air calcination at 853 K to remove the organic structure directing agent used for its crystallisation (4-cyclohexyl-1,1-dimethylpiperazinium). The integrity of the sample used in this study was checked by means of X-ray diffraction and micropore volume determination from the N_2 adsorption isotherm at 77 K. Both techniques show that the structural integrity of the zeolite is preserved upon organic removal by calcination. C_3 and linear C_4 hydrocarbons adsorption isotherms and kinetic measurements were performed in an IGA-3 gravimetric analyser (Hiden Isochema). Approximately 50 mg of the calcined sample were placed in the balance. Before each adsorption experiment, the sample was outgassed at 673 K under a final pressure of 10^{-5} Pa during four hours to fully remove any adsorbant from its pore volume. No weight modification was observed at the end of this pre-treatment. The temperature of the sample was subsequently reduced under high vacuum until the target temperature (from 298 to 393 K) for each adsorption experiment was reached. Adsorption measurements were performed by introducing gas to build up the desired pressures. Typically, 26 equilibrium data points up to 91.2 KPa were recorded for each gas and adsorption temperature in order to build the isotherms, whereas the kinetic experiments were performed at pressures of 30.4 KPa. The equilibrium conditions were fixed at 98% of the calculated uptake using the Avrami–Erofe'ev model[18] or a maximum equilibration time of 120 minutes for each point of the isotherms, while the kinetic measurements were conducted up to 72 hours.

The Langmuir model failed to fit properly the adsorption isotherms of propene and *trans*-2-butene in ITQ-32, but they were successfully fitted using the Dual-Site Langmuir (DSL)[19] and Toth[20] models, which take into account the heterogeneity in the adsorption sites. These models were previously used for olefin and paraffin adsorption studies on 8-membered ring zeolites.[9,21,22] Unfortunately, the thermodynamic constants derived from these models when applied to the adsorption isotherms of ITQ-32 were not satisfactory. Also, a good fit was obtained by applying the Dubinin–Astakhov formalism[23,24] (see Figs. 1 and 2 in the supplementary information) and the derived thermodynamic constants had more physical sense than those obtained using the above mentioned models. These final Dubinin adsorption parameters are given in Table 1 of the supplementary information.

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It should be noted that propane, butane, 1-butene and *cis*-2-butene adsorption measurements at the experimental conditions used in this work did not reach equilibrium at any temperature. Indeed, the uptake of these gases increases with temperature, indicating that there are strong diffusional restrictions to them filling up the empty volume of ITQ-32 zeolite. This has been further proved by performing the propane adsorption experiment at 393 K, where lower diffusional limitations should be expected, but using a very long equilibration time (4 hours). When this is done, it is observed that the adsorption capacity increases by 15% with respect to a similar experiment using 2 hours for equilibrium (see Fig. 3 in the supplementary material). Since much higher uptakes of propene and *trans*-2-butene than other C_3 and C_4 hydrocarbons were observed and much shorter times to achieve the equilibrium, ITQ-32 appeared as a promising material for separation of propene and *trans*-2-butene from the steam reforming stream. To do that, diffusional studies were performed at 30.4 KPa of pressure and the gas uptake was continuously monitored *versus* time.

When crystals are not of uniform size and geometry, as in our case, the diffusion ability of a particular gas or vapour within a porous crystalline material is usually measured in terms of its characteristic D/r^2 values, which are the inverse of the diffusion times. In this parameter, D is the Fickian diffusion coefficient and r is the averaged radius representative of the crystal size distribution of the adsorbant. D/r^2 can be derived from adsorption kinetic measurements by applying the Crank solution for diffusion[25] with a simplification of this equation for short times.[26] However, in our experimental conditions the adsorption rate of olefins in the early stages is limited by the pressure ramp that can be achieved in the gravimetric microbalance and, therefore, the short time simplification cannot be accurately applied. For this reason, the complete equation has been used for the determination of parameter D/r^2 (eq. 1),[25]where Q represents the gas uptake at a time t and Q_∞ the uptake at the equilibrium.

$$\frac{Q}{Q_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2\pi^2 t\frac{D}{r^2}\right) \qquad (1)$$

It has been reported that to achieve effective gas separations the ratio of the diffusion coefficients (R_D) between the gas that is adsorbed the fastest and the following one must be at least 50.[10] Then, as a first rough approximation, the R_D values for pure silica ITQ-32 have been calculated by applying equation (1) and assuming that Q_∞ for the slowest C_3 and C_4 adsorbates will not significantly differ from the Q_∞ of propene and *trans*-2-butene, respectively.

The ability of ITQ-32 to separate propene and propane can be deduced from the results shown in Table 1, where the D/r^2 parameters calculated using equation (1), as well as the ratio of the diffusion coefficients of propene and propane (R_D), are presented. Also, the adsorption rates of propene and propane in ITQ-32 at 333 K are compared in Fig. 4 of the supplementary material. The R_D parameter varies with temperature, being close to 1500 at 298 and 333 K, decreasing to 580 at 363 K. These results clearly indicate that ITQ-32 zeolite is a good candidate for carrying out separations of propene–propane gas mixtures.

Table 1 D/r^2 coefficients for propene and propane adsorption in ITQ-32 zeolite at 30.4 KPa and different temperatures, calculated using equation (1)

	D/r^2 (s^{-1})		
	298 K	333 K	363 K
propene	3.86×10^{-5}	1.06×10^{-4}	2.06×10^{-4}
propane[a]	2.70×10^{-8}	6.58×10^{-8}	3.55×10^{-7}
R_D[b]	1430	1611	580

[a] Fitting of equation (1) was done assuming that Q_∞ of propane was the same as that of propene. [b] R_D is calculated as the ratio of diffusion of propene to propane.

To our knowledge, pure silica chabazite[10,11] and ITQ-12[27] are the most successful zeolites for propene–propane separation. ITQ-12 allows thermodynamic propene–propane separation, which is the preferred performance for gas separation. But, the adsorption capacity and especially the slow kinetics of propene adsorption should be considered for its commercial application. On the other hand, chabazite has shown an exceptional behaviour for carrying out kinetically based propane–propene separation. Then, the propane–propene separation abilities of pure silica chabazite (prepared as reported in ref. 11) and ITQ-32 zeolite were studied using the same experimental conditions. The comparison of R_D parameters calculated for chabazite and ITQ-32 is given in Table 2 of the supplementary information. There, it is seen that chabazite performs much better in the separation of propene and propane than ITQ-32 zeolite at low temperature, but this difference is reduced when the temperature increases.

These results encouraged us to extend this study to linear C_4 hydrocarbons. The uptake plots at 298 and 333 K of butane, 1-butene, *cis*-2-butene and *trans*-2-butene in ITQ-32 zeolite are presented in Fig. 1, and the corresponding calculated diffusion coefficients at different temperatures are reported in Table 2. From these results, it is evident that *trans*-2-butene diffuses the fastest, followed by 1-butene, which presents an intermediate diffusion coefficient. Finally, the lowest diffusion rates were obtained for butane and *cis*-2-butene, which practically are not adsorbed at 333 K. The ratio of the diffusion parameters (R_D) of *trans*-2-butene and 1-butene at 298 K is around 500, evidencing the capability of ITQ-32 for separation of these gases at room temperature.

Interestingly, the diffusion parameter of 1-butene is 175 times larger than that calculated for butane at room temperature, indicating that 1-butene can also be separated from butane. However, the kinetics of 1-butene adsorption on ITQ-32 at 298 K is too slow to be applicable for 1-butene–butane separation. But considering that the R_D coefficient between 1-butene and butane remains in values higher than 50 up to at least 363 K (see Table 2), which is the maximum temperature studied in this work, and the diffusion rate for 1-butene in ITQ-32 grows rapidly, it seems feasible to perform 1-butene–butane separation at relatively high temperatures using ITQ-32. Finally, it should be noted that the diffusion coefficient of *cis*-2-butene is close to that of butane and therefore, the discussion given for 1-butene–butane separation stands for 1-butene–*cis*-2-butene separation.

Also, non-charged chabazite materials have been used for C_4 separations[28] and, consequently, we have performed comparative diffusion experiments (see Fig. 5 and Table 3 in the supplementary information) using pure silica chabazite. It is possible to separate *trans*-2-butene from the remaining C_4, but there is no chance of

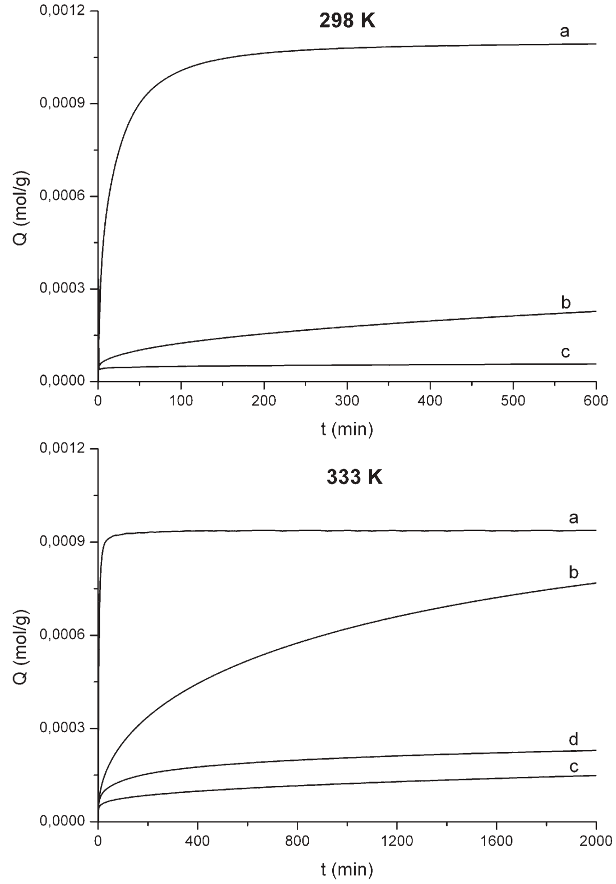

Fig. 1 Adsorption kinetics of C_4 hydrocarbons at 298 and 333 K and 30.4 KPa in ITQ-32. *trans*-2-butene (a), 1-butene (b), butane (c) and *cis*-2-butene (d).

Table 2 D/r^2 parameters for *trans*-2-butene, 1-butene, *cis*-2-butene and butane adsorption in ITQ-32 zeolite at 30.4 KPa and different temperatures, calculated using equation (1)

	D/r^2 $(s^{-1})^a$		
	298 K	333 K	363 K
trans-2-butene	4.73×10^{-5}	2.46×10^{-4}	4.64×10^{-4}
1-butene	9.71×10^{-8}	1.10×10^{-6}	5.33×10^{-6} [b]
cis-2-butene	—	6.26×10^{-8}	—
butane	5.61×10^{-10}	1.79×10^{-8}	7.84×10^{-8}

[a] Fitting of equation (1) was done assuming that Q_∞ of C_4 was the same as that of *trans*-2-butene. [b] Fitting of equation (1) was done assuming its own Q_∞ instead of that of *trans*-2-butene.

carrying out the separation of 1-butene from butane, and the aluminophosphate AlPO-34, which is isostructural to chabazite, must be employed for this purpose.[28] Therefore, ITQ-32 possesses a micropore topology which is in between that of ITQ-12 and chabazite, allowing the separation of *trans*-2-butene at any temperature and 1-butene at relatively high temperatures.

It must be said that ITQ-32 is very stable to repeated adsorption cycles and after 20 adsorption–desorption cycles we did not observe any olefin oligomerisation being produced, while the initial adsorption capacity was maintained.

Therefore, it seems feasible to design a double pressure swing adsorption process based on ITQ-32 zeolite that can afford the effective separation of *trans*-2-butene and 1-butene from the linear C_4 hydrocarbon fraction coming from the steam reformer by controlling the process temperature. These consecutive separations can be afforded attending to diffusion coefficients given in Table 2.

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Notes and references

1 G. E. Keller, A. E. Marcinkowsky, S. K. Verma and K. D. Williamson, in *Separation and Purification Technology*, ed. N. N. Li and J. M. Calo, Marcel Dekker, New York, 1992.
2 R. B. Eldridge, *Ind. Eng. Chem. Res.*, 1993, **32**, 2208.
3 K. G. Strohmaier and D. E. W. Vaughan, *J. Am. Chem. Soc.*, 2003, **125**, 16035.
4 J. L. Paillaud, B. Harbuzaru, J. Patarin and N. Bats, *Science*, 2004, **301**, 990.
5 A. Corma, M. J. Díaz-Cabañas, F. Rey, S. Nicolopoulus and K. Boulahya, *Chem. Commun.*, 2004, **12**, 1356.
6 A. Corma, M. J. Díaz-Cabañas, J. L. Jordá, C. Martinez and M. Moliner, *Nature*, 2006, **443**, 842.
7 S. U. Rege, J. Padin and R. T. Yang, *AIChE J.*, 1998, **44**, 799.
8 W. Zhu, F. Kapteijn and J. A. Moulijn, *Chem. Commun.*, 1999, 2453.
9 W. Zhu, F. Kapteijn, J. A. Moulijn, M. C. Exster and J. C. Jansen, *Langmuir*, 2000, **16**, 3322.
10 D. H. Olson, *U.S. Pat.*, 2002/0144597, 2002.
11 D. H. Olson, M. A. Camblor, L. A. Villaescusa and G. H. Kuehl, *Microporous Mesoporous Mater.*, 2004, **67**, 27.
12 L. S. Cheng and S. T. Wilson, *U.S. Pat.*, 6293999, 2001.
13 S. C. Reyes, V. Krishnan, G. J. De Martin, J. H. Sinfelt, K. G. Strohmaier and J. G. Santiesteban, *WO Pat.*, 03/080548, 2003.
14 D. J. Safarik and R. B. Eldridge, *Ind. Eng. Chem. Res.*, 1998, **37**, 2571.
15 N. Hedin, G. J. DeMartin, K. G. Strohmaier and S. C. Reyes, *Microporous Mesoporous Mater.*, 2007, **98**, 182.
16 R. M. Barrer, in *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, 1978.
17 A. Cantín, A. Corma, S. Leiva, F. Rey, J. Rius and S. Valencia, *J. Am. Chem. Soc.*, 2005, **127**, 11560.
18 B. V. Erofe'ev and C. R. Dokl, *Acad. Sci., USSR*, 1946, **52**, 511.
19 I. H. Doetsch, D. M. Ruthven and K. F. Loughlin, *Can. J. Chem.*, 1974, **52**, 2117.
20 J. Toth, *Acta Chim. Acad. Sci. Hung.*, 1971, **69**, 311.
21 W. Zhu, F. Kapteijn and J. A. Moulijn, *Stud. Surf. Sci. Catal.*, 2001, **135**, 2961.
22 C. A. Grande, C. Gigola and A. E. Rodrigues, *Ind. Eng. Chem. Res.*, 2002, **41**, 85.
23 M. M. Dubinin, V. A. Astakhov and L. V. Radushkevich, in *Physical Adsorption of Gases and Vapors in Micropores, Progress and Membrane Science*, Vol. 9, Academic Press, New York, 1975, pp. 1–70.
24 C. A. Grande, C. Gigola and A. E. Rodrigues, *Adsorption*, 2003, **9**, 321.
25 J. Crank, in *The Mathematics of Diffusion*, Oxford University Press, London, 1957.
26 J. Kärger and D. M. Ruthven, in *Diffusion in Zeolites and Other Microporous Solids*, John Wiley & Sons, New York, 1992.
27 D. H. Olson, X. Yang and M. A. Camblor, *J. Phys. Chem. B*, 2004, **108**, 11044.
28 G. L. Casty, R. H. Hall, S. C. Reyes, R. P. Reynolds and K. G. Strohmaier, *U.S. Pat.*, 2004/026138, 2004.