Length exclusion in the adsorption of chain molecules on chabazite type zeolites

Inge Daems,[a] Ranjeet Singh,[b] Gino Baron[a] and Joeri Denayer*[a]

Received (in Cambridge, UK) 30th October 2006, Accepted 7th December 2006
First published as an Advance Article on the web 10th January 2007
DOI: 10.1039/b615661d

In the adsorption of linear C_1–C_8 alkanes, alkenes and alcohols on zeolite chabazite, molecules smaller than 6.7 Å are adsorbed in significant amounts, whereas longer chains are almost fully excluded from the micropores.

The shape selective properties of zeolites are at the basis of their success in catalytic, ion exchange and adsorption processes. The molecular sized pores of zeolites impose steric constraints on the adsorption, diffusion and catalytic conversion of larger species. One of the most known examples hereof is the separation of non-linear and linear hydrocarbons by complete exclusion of branched chains from the narrow sized pores of zeolite 5A for the production of solvents, biodegradable detergents and plasticisers.[1] For linear alkane chains, the affinity for adsorption typically increases with chain length as the total interaction between the alkane and the zeolite increases with the number of interacting atoms.[2–6] Linear alkanes of different chain length all have the same molecular diameter and thus experience a similar steric constraint when diffusing through tubular zeolite pores.

We measured the adsorption of linear alkanes, 1-alkenes and 1-alcohols containing up to 8 C-atoms on chabazite (CHA) zeolite in gas and liquid phase conditions. CHA (Fig. 1) has a three dimensional pore system with ellipsoidal shaped cages (6.7 × 10 Å) that are accessible *via* 8 membered ring windows (3.8 × 4.2 Å) (Fig. 1).

Chabazite was synthesized following the procedure reported by M. Bourgogne *et al.* with gel composition 0.17 Na_2O : 2.0 K_2O : 5.18 SiO_2 : Al_2O_3 : 224 H_2O.[7] The composition of the unit cell of the tested sample, measured by ICP, was $Na_{0.8}K_{9.5}[Al_{10.3}Si_{25.7}O_{72}]$. The crystals had an irregular disc-shape with a mean diameter of 1 μm. The Dubinin micropore volume and surface area of the CHA sample as determined by N_2-porosimetry were 0.17 ml g^{-1} and 486 m^2 g^{-1}.

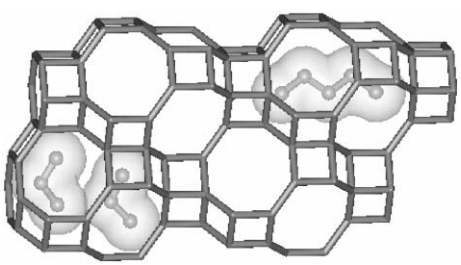

Fig. 1 Structural framework of CHA-type zeolite with its ellipsoidal cages containing pentane and propane.

Equilibrium adsorption isotherms of CH_4, C_2H_6, C_2H_4 and C_3H_8, were determined using the volumetric technique at 299 K after zeolite activation at 623 K. The adsorption of methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, pentane, hexane, heptane, octane and octene on chabazite was determined at 299 K in liquid phase using a batch adsorption technique.†

Fig. 2 shows the maximum adsorption capacity of all studied alcohols and alkanes expressed in adsorbed molecules per cage and C-atoms per cage. The highest adsorption capacities are attained for the alcohols, strongly interacting with this relatively polar zeolite. About 10 molecules of the smallest alcohol, methanol, are adsorbed per chabazite cage. This highly polar component is able to fill the entire micropore volume, 0.17 ml g^{-1}. With increasing chain length, the number of adsorbed alcohol molecules decreases. This decrease in capacity is very drastic in the C_1–C_3 range. While a cage can still contain 1 propanol or butanol molecule, remarkably, alcohols larger than butanol are adsorbed in very low amounts (<6% of the available pore space).

Compared to the alcohols, the number of n-alkane molecules adsorbed per cage decreases more gradually with their increasing chain length. While 6 methane molecules are hosted per single cage, the maximum adsorption capacity for octane amounts only 0.16 molecules per cage. The adsorption capacity for pentane is observed to be exactly 1 molecule per cage. At this pore occupancy each gram zeolite contains 0.048 ml pentane, meaning pentane is only able to fill ~30% of the available micropore volume. This can be understood based on the relationship between the cage dimension and molecular size. In its stretched configuration pentane has a chain length (8.84 Å)[8] that is only slightly smaller than the length of the ellipsoid shaped cages (10 Å). Besides, the cages are too narrow to contain 2 pentane molecules having each a diameter of 4.3 Å, next to each other. This way chabazite cages simply can not host more than 1 axialy positioned pentane molecule (Fig. 1). Hexane, heptane and octane having chain lengths of respectively 10.11, 11.38 and 12.65 Å do not even fit inside a single cage and have to overcome the large energy barriers generated by the small windows. This is energetically very unfavorable, causing exclusion of alkanes larger than pentane from the zeolite cages. These experimental data do not support results of molecular simulations[9] predicting adsorption of linear alkanes containing up to 11 C-atoms in a highly coiled

[a]*Dienst Chemische Ingenieurstechniek, Vrije universiteit Brussel, Pleinlaan 2, B-1050, Brussels, Belgium. E-mail: Joeri.Denayer@vub.ac.be; Fax: +32 2 629 32 48; Tel: +32 2 629 17 98*
[b]*Department of Chemical Engineering, Monash University, PO Box 36, Clayton Victoria, 3800, Australia. E-mail: ranjeet.singh@eng.monash.edu.au; Fax: +61-3-99055686; Tel: +61-3-99052632*

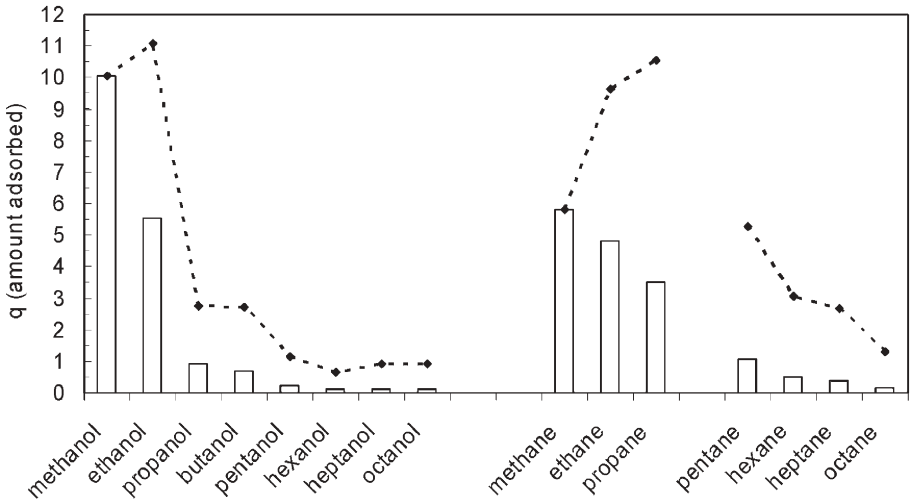

Fig. 2 Adsorption capacities of 1-alcohols and *n*-alkanes on CHA in liquid phase at 299 K. The bars and line graphs give the number of molecules and C-atoms adsorbed per cage respectively.

conformation inside a single CHA cage. However, the results given in Fig. 2 do show a single cage can contain as much as 5.5 ethanol or 3.5 propane molecules, corresponding to respectively 11 and 10.5 C-atoms. In order to reach such dense packing, the molecules have to be stacked inside the cage in a very specific way. Ethanol and propane have chain lengths (5.6 and 6.3 Å) which are slightly smaller than the width of the cage (6.7 Å). This way these molecules can adsorb with their main carbon chain perpendicular to the length axis of the cage (Fig. 1).

For alcohols the capacity cut-off already occurs between ethanol and propanol. The chain length of propanol (6.9 Å) only allows the molecule to be positioned according to the longitudinal axis of the cage.

A limited number of experiments was performed using 1-alkenes as adsorbates. Also here a similar adsorption behaviour was observed. While small alkenes were able to fill the micropores (*e.g.* ethene: 6.3 molecules/cage or 12.6 C-atoms/cage), longer alkenes were almost completely excluded from the micropores (*e.g.* 1-octene: 0.2 molecules/cage or 1.6 C-atoms/cage).

The adsorption of mixtures of linear molecules on CHA was studied by measuring the competitive adsorption of a series of binary ethanol–hexanol mixtures (Fig. 3). Over the whole composition range, ethanol is selectively removed from the mixture by adsorption in the zeolite whilst hexanol is not adsorbed at all and remains in the liquid mixture. The selectivity diagram clearly shows an almost 100% selectivity for ethanol up to a hexanol mole fraction of 0.85 in the external liquid phase. This means a better fitting in the internal zeolite pores not only leads to a higher adsorption capacity but also a higher selectivity of the shorter linear molecules.

Up to now all experimental or simulation work[10–13] on CHA type zeolite only focused on the adsorption of small molecules, *e.g.* N_2, CH_4, O_2, CH_3CN, CO, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and CH_3OH. The results presented in this article shed a new light on the applicability of CHA-type zeolites. Whereas typical zeolites with tubular pores preferentially adsorb long chain over short chain molecules, CHA operates in the opposite way and excludes longer chains from adsorption. This cage/window type zeolite can be used to separate short from long chain linear molecules by selective adsorption of the short molecules. CHA could also be applied in purification processes in which traces of small molecules have to be removed from mixtures of heavier components which is very difficult to realize *via* distillation. The principle of length exclusion as presented here could be extended to other product fractions by tailor made design of zeolites with larger cages than CHA interconnected *via* small windows.

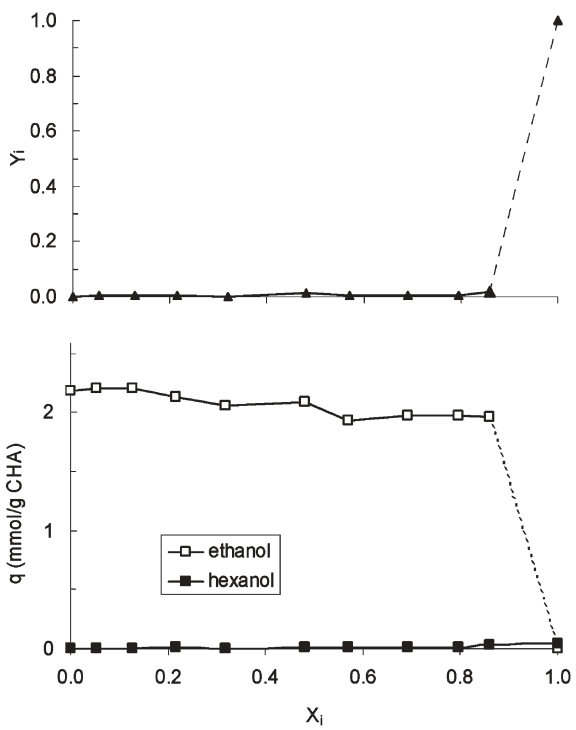

Fig. 3 Binary adsorption isotherm (lower graph) and selectivity diagram (upper graph) of an ethanol–hexanol mixture on CHA in liquid phase at 299 K (X_i and Y_i: external and internal molefraction longest molecule).

This research was financially supported by FWO Vlaanderen (G.0127.99). Denayer is grateful to the F.W.O.-Vlaanderen for a fellowship as postdoctoral researcher.

Notes and references

† In the liquid phase batch experiments[8] *iso*-octane was used as a non-adsorbing solvent except for the adsorption of methanol, where *tert*-butanol was used as non-adsorbing solvent.

1 S. Kulprathipanja and J. A. Johnson, in *Handbook of Porous Solids*, ed. F. Schüth, K. S. W. Sing and J. Weitkamp, Wiley-VCH, Weinheim, 2002, p. 2568.
2 A. Atkinson and G. Curthoys, *J. Chem. Soc., Faraday Trans.*, 1981, **77**, 897.
3 A. P. Vavlitis, D. M. Ruthven and K. F. Loughlin, *J. Colloid Interface Sci.*, 1981, **84**, 526.
4 H. Stach, U. Lohse, H. Thamm and W. Schirmer, *Zeolites*, 1986, **6**, 74.
5 J. F. M. Denayer and G. V. Baron, *Adsorption*, 1997, **3**, 251.
6 F. Eder and J. A. Lercher, *Zeolites*, 1997, **18**, 75.
7 M. Bourgogne, J. L. Guth and R. Wey, U.S. Patent 4503024, 1985.
8 K. M. A. De Meyer, S. Chempath, J. F. M. Denayer, J. A. Martens, R. Q. Snurr and G. V. Baron, *J. Phys. Chem. B*, 2003, **107**, 10760.
9 D. Dubbeldam and B. Smit, *J. Phys. Chem. B*, 2003, **107**, 12138.
10 A. R. George, C. R. A. Catlow and J. M. Thomas, *Microporous Mater.*, 1997, **11**, 97.
11 L. Yang, K. Trafford, O. Kresnawahjuesa, J. Sepa, R. J. Gorte and D. White, *J. Phys. Chem. B*, 2001, **105**, 6874.
12 V. V. Milhaleva, R. A. van Santen and A. P. J. Jansen, *J. Phys. Chem. B*, 2001, **105**, 6874.
13 D. H. Olson, M. A. Camblor, L. A. Villaescusa and G. H. Kuehl, *Microporous Mesoporous Mater.*, 2004, **67**, 27.

