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Shape selectivity in the adsorption of propane/propene on the all-silica DD3R

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High adsorption selectivity for propene suggests that the all-silica DD3R might be effective as an adsorbent for the separation or purification of propene and propane mixtures.

Cryogenic distillation has been the dominant technology utilized for propane/propene separations for many years. Although traditional distillation is reliable and essentially unchallenged in this application, the necessary low temperatures and high pressures make it an energy-intensive separation scheme because of the small difference in their relative volatilities.[1]

A process configuration based on a hybrid adsorption/distillation system has been proposed to be an attractive commercial arrangement.[2] In order to achieve this objective, it is of utmost importance to find an effective adsorbent. Commercial zeolites (13X, 5A and 4A) and some Ag^+-substituted resins and $CuCl/\gamma$-Al_2O_3 have been investigated.[3–6] Such adsorbents show high selectivity for propene over propane.

Regeneration of zeolite-based adsorbents is difficult in applied vacuum swing adsorption (VAS) processes at temperatures as low as 298 K.[6] Increasing the operating temperature can improve this, but high temperatures can lead to propene oligomerization and possibly cracking owing to catalytic action of these materials, eventually blocking the adsorbents. In addition, these hydrophilic zeolites are sensitive to moisture.[2] Separations by adsorption *via* π-complexation are susceptible to deactivation by feed contaminants.[1]

Here, we demonstrate the selective adsorption of propene/propane on the all-silica DD3R, a highly hydrophobic and inert adsorbent, which is stable up to high temperatures.

Deca-dodecasil 3R (DD3R) is a member of the clathrasil family possessing topologically different frameworks. Gies[7] did pioneering work on the synthesis of the clathrasil DD3R. An optimum procedure for the clathrasil DD3R crystallization that ensures the phase purity of DD3R has been developed for scale-up by Den Exter *et al.*[8] The accessible pore space consists of 19-hedron cavities, connected *via* windows consisting of eight oxygen anions. Each cavity is connected to three other cavities in a hexagonal planar arrangement.[9]

The all-silica DD3R crystals had been synthesized in-house.[8] The template inside the clathrasil DD3R crystals was removed by calcination at 973 K for 6 h. The apparent density of the all-silica DD3R was 1.714 g cm^{-3} and the adsorption of N_2 indicated an accessible microporous void volume of 0.15 cm^3 g^{-1}. The crystal size was in the range of 5–10 μm as determined by SEM.

A Rupprecht & Patashnick TEOM 1500 mass analyzer with 100 mg sample size was used in an experimental set-up designed for measurement of equilibrium and transient adsorption on microporous materials.[10]

Prior to the experiments the crystals were outgassed in a helium flow of 200 cm^3 min^{-1} at 573 K for 24 h in order to remove adsorbed impurities. Helium was obtained as an ultra-high purity gas (> 99.999%). Propane and propene were 3.5 grade (> 99.95%).

The difference in the adsorption behavior between propane and propene is shown in Fig 1. The mass uptake for propane is much lower than that for propene under the same conditions. Fig. 1 also shows the mass uptake of binary mixture of propane and propene, which is the same as that of propene at the same partial pressure. This indicates that the presence of propane hardly affects the adsorption of propene.

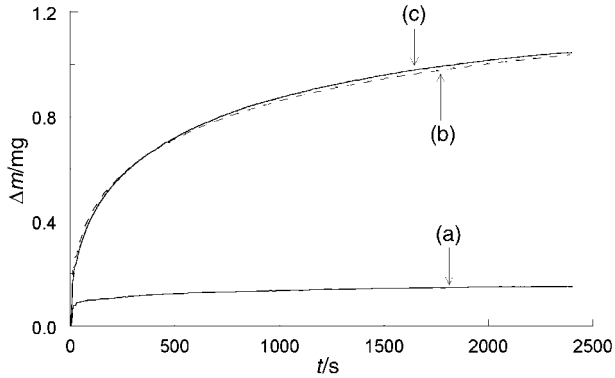

Fig. 1 Mass uptakes of single components, propane and propene, and their mixture in flowing He at a total pressure of 101.3 kPa and 373 K. A sample of 48.7 mg of the all-silica-DD3R was used in the TEOM. (a) propane (25 kPa), (b) propene (25 kPa) and (c) propane (25 kPa)–propene (25 kPa).

The critical diameter of propene (see Table 1) is significantly smaller than the free cross diameter of the 8-ring window (0.45 nm) and their molecules can enter into the 19-hedron cavities. However, the critical diameter of propane is close to 0.45 nm, so it can be expected that propane molecules are restricted from entering the 19-hedron cavities. The results shown in Fig. 1 indicate that the 8-ring window cavities are accessible to propene, while they exclude propane molecules. The small amount adsorbed for propane is attributed to adsorption at the external surface of the DD3R crystals.

Table 1 Characteristic diameters of the adsorbate molecules studied

Adsorbate	σ_s[a]/nm	σ_C[b]/nm
Propane	0.280	0.446
Propene	0.265	0.431

[a] Structural diameter defined as the diameter of the smallest cylinder that can be drawn around the molecule in its most favorable conformation through the centers of the extreme binding atoms.[11] [b] Critical diameter calculated by the summation of the structural diameter and the effective van der Waals radii of two extreme hydrogen atoms.

It takes a long time for the uptake of propene to reach the equilibrium state. This phenomenon can be interpreted in terms of the accessibility of the cavities to the adsorbate molecules. The orientation of the molecules to enter the 8-ring window and to move to the next cavity will play a role. Such a diffusion resistance can be improved by increasing the operating temperature.

The isotherms of propene on the all-silica DD3R at a temperature between 303 and 473 K are shown in Fig. 2 where closed symbols represent desorption. The isotherms were reversible over the complete pressure range investigated, resulting in the overlay of the adsorption and desorption

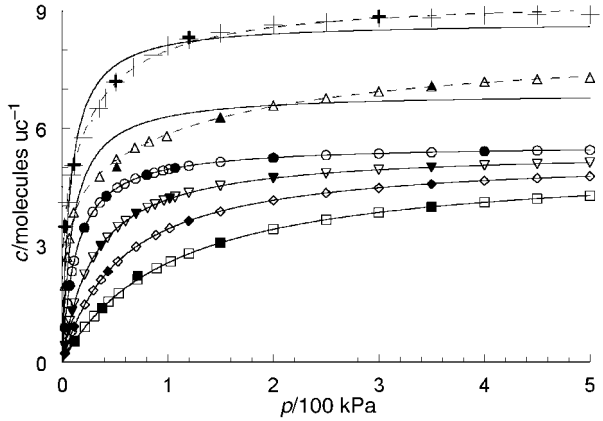

Fig. 2 Isotherms of propene on the all-silica DD3R. Open symbols adsorption data and closed symbols desorption data, solid lines Langmuir isotherm model fits and dashed lines dual-site Langmuir isotherm model fits; (+) 303 K, (▲) 338 K, (●) 373 K, (▼) 408 K,(◆) 438 K, (■) 473 K.

isotherms in Fig. 2. The isotherm data of propene are well described by the Langmuir model at high temperatures. However, deviations from the Langmuir model have been observed at 303 and 338 K and the higher-pressure range, at which the amount adsorbed exceeds six molecules per unit cell, corresponding to one molecule per cavity. These deviations from the Langmuir model are attributed to interactions between adsorbates as the number of molecules sitting inside the 19-hedron cavity exceeds one. The isotherm data at 303 and 338 K are better fitted by the dual-site Langmuir model (DSL). This DSL model takes into account implicitly interactions between adsorbates, which give rise to a pseudo-second adsorption site.

Various experimental results reveal high selectivity for propene on the all-silica DD3R. This adsorbent does not show any catalytic activity to hydrocarbons over a wide range of temperature. Furthermore, water hardly adsorbs on this material. In conclusion, the all-silica DD3R is an effective shape-selective adsorbent for the separation or purification of propane–propene mixtures. Its potential application in separation is being further investigated.

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