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Accelerated synthesis of all-silica DD3R and its performance in the separation of propylene/propane mixtures

Jorge Gascon *, Wouter Blom, Arjen van Miltenburg, Alexandre Ferreira, Rob Berger, Freek Kapteijn

Delft University of Technology, Catalysis Engineering Group, Julianalaan 136, 2628 BL Delft, The Netherlands

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ABSTRACT

Synthesis of the all-silica Deca-Dodecasil 3 Rhombohedral (DD3R) zeolite was accelerated 10 times by seeding with small amount of crystals (0.02 wt%) with yields approaching 100%. The effects of other synthesis variables, like silica source, the presence of methanol or the synthesis pH on the final product distribution have been studied. The adsorption and separation of propylene and propane mixtures on this material are presented. The improved synthesis may form the basis to scale-up production of DD3R for selective separation processes. The single component adsorption isotherms could be well described with a dual-site Langmuir model. The binary mixture adsorption was determined from breakthrough/desorption experiments at 323, 358 and 383 K. By modelling the adsorptive column, diffusion coefficients at infinite dilution for single component and the effect of propane over propylene adsorption were determined. Cylindrical geometry describes the pore topology of DDR type materials well. Propane decreases the uptake rate of propylene by adsorption in the surface of the crystals. Propylene diffusion is best described by the "strong confinement" model inside the zeolite cages. Separation is due to only propylene adsorption with diffusion as rate determining step.

Results revealed DD3R as a very effective molecular sieve for the separation or purification of propane–propylene mixtures.

1. Introduction

The continuing rise of crude oil prices together with the pressure to reduce greenhouse gas emissions drive industry to be more energy efficient. Therefore, the need to identify more energy efficient separation techniques rises every day.

Distillation has always been the prime process used to separate most of the naphtha products. The columns to separate the olefins from the paraffin's of the C2, C3 and C4 components are among the most energy intensive distillation applications in oil refining. The olefin/paraffin separation makes up almost 7% of the total distillation energy demand of the USA [1]. The smaller the molecules to be separated, the larger the energy demand of the process: propane–propylene separation takes place in a distillation tower consisting of over 100 trays. The energy demand of this distillation represents up to 85% of the total costs of the entire process [2].

In new technologies such as catalytic dehydrogenation to produce olefins [3], single pass conversions are low and limited by the thermodynamic equilibrium to a conversion of 20–40%. In order to obtain the olefin and for the complete dehydrogenation of the paraffin feed, separation of the mixtures is required.

Physical/chemical adsorption appears to be the most attractive alternative, because of the maturity of the basic technology, the available adsorbents, and low-cost, low-energy but highly efficient gas separation system [4]. Hybrid methods that combine the traditional distillation and adsorption processes have been proposed as an economical alternative [5,6]. The basic idea is to carry out the most difficult separation (paraffin/olefins) by adsorption, to eliminate this energy-intensive and expensive olefin-alkane distillation step.

Some patents have been already claimed for the separation of propane/propylene mixtures using adsorptive methods [7]. Commercial zeolites (13X, 5A and 4A), some Ag^+-substituted resins, Titanosilicates or mesoporous SBA-15, AlPO-14, CuCl/α-Al_2O_3, carbon molecular sieves or CuCl/FAU have been investigated [1,5,8–13]. Such adsorbents show high selectivity for propylene over propane. Regeneration of zeolite-based adsorbents is difficult in the applied vacuum swing adsorption (VSA) processes that operate at temperatures as low as 298 K [4]. Increasing the operating temperature can improve this, but high temperatures can lead to propylene oligomerization and possibly cracking by catalytic action of these materials, eventually blocking the adsorbents [14]. In addition, these hydrophilic zeolites are sensitive to moisture. Separations by adsorption via π-complexation are susceptible to deactivation by feed contaminants [15]. Preferred sorbents should

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* Corresponding author.
E-mail address: j.gascon@tudelft.nl (J. Gascon).

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Notation

A_{cr}	surface area of one side of the crystallite [m^2]
A_{cross}	cross-sectional area of the bed [m^2]
C_i	concentration of i that can be adsorbed [mol-i m^{-3}]
$C_{i,\mathrm{b}}$	concentration of i in the bulk [mol-i m^{-3}]
$C_{i,\mathrm{s}}$	concentration of i at the external surface [mol-i m^{-3}]
$C^*_{i,\mathrm{s}}$	concentration of i at pore entrances (‘gates’) [bar]
D_i	dispersion coefficient of A in the bed [$\mathrm{m}^2\ \mathrm{s}^{-1}$]
Đ_i	diffusivity of i in zeolite (at infinite dilution) [m^{2-1}]
$\text{Đ}_{i,0}$	diffusivity of i in zeolite at zero loading [m^{2-1}]
$\text{Đ}_{i,T_{\mathrm{ref}}}$	diffusivity of i in zeolite at reference temperature [m^{2-1}]
$D_{i,\mathrm{ax}}$	axial dispersion coefficient of i $\left(\frac{D_i}{\varepsilon_\mathrm{b}} = \frac{D_{i,m}}{\tau_\mathrm{b}} + md_p u_0\right)$[40] [$\mathrm{m}^2\ \mathrm{s}^{-1}$]
$D_{i,m}$	bulk diffusivity of i [$\mathrm{m}^2\ \mathrm{s}^{-1}$]
d_{cr}	crystallite thickness (or diameter) [m]
d_{p}	particle diameter [m]
E_{a}	activation energy [J mol^{-1}]
F_i	volumetric flowrate of component i into the column [ml min^{-1}]
h	local height [m]
h_{b}	total bed height [m]
ΔH^i	adsorption enthalpy for site i [J mol^{-1}]
$k_{\mathrm{G},i}$	mass transfer coefficient from bulk to crystallite [m/s]
K_i	adsorption constant of component i [bar^{-1}]
$K_{i,\mathrm{s}}$	external surface adsorption constant of component i [bar^{-1}]
L_{cr}	crystallite length [m]
N_{pp}	number of adsorbent particles per unit of bed volume [m^{-3}]
p_i	partial pressure of i [bar]
$p_{i,\mathrm{b}}$	bulk partial pressure of i [bar]
$p_{i,\mathrm{s}}$	partial pressure of i at external surface of crystallites [bar]
$p^*_{i,\mathrm{s}}$	partial pressure of i at pore entrances (‘gates’) [bar]
q_i	loading with component i [mol-i kg-$\mathrm{zeolite}^{-1}$]
q_i^{sat}	saturation loading i (at infinite partial pressure) [mol-i kg-$\mathrm{zeolite}^{-1}$]
r	spatial coordinate inside the zeolite crystallites [m]
Re_{p}	particle Reynolds number ($=\rho_\mathrm{G}\ u_0\ d_\mathrm{p}/\ \mu_\mathrm{G}$) [–]
Sc_i	Schmidt number for component A ($=\mu_\mathrm{G}/(\rho_\mathrm{G}D_{i,m})$) [–]
Sh_i	Sherwood number for component A ($=k_{\mathrm{G},i}d_\mathrm{p}/D_{i,m}$) [–]
t	time [s]
u_0	superficial linear velocity (=velocity without pellets) [m s^{-1}]
W_{ads}	total weight of adsorbent (zeolite crystals) [kg]
z	dimensionless axial position in the bed [–]
γ	‘gate factor’, see Eq. (11) [–]
ε_{b}	bed porosity [m^3-void (m^3-bed)$^{-1}$]
Γ_i	thermodynamic (correction) factor for adsorption of i [–]
∂	differential operator
θ_i	relative surface coverage by component i [–]
ρ_{cr}	zeolite crystallite density (1740 $\mathrm{kg/m}^3$ for DD3R [22]) [kg m^{-3}]
ρ_{G}	gas density [kg m^{-3}]
μ_{G}	gas viscosity [kg $\mathrm{m}^{-1}\ \mathrm{s}^{-1}$]
τ_{b}	bed tortuosity ($\tau_\mathrm{b} = 1/\sqrt{\varepsilon_\mathrm{b}}$) [kg $\mathrm{m}^{-1}\ \mathrm{s}^{-1}$]
ξ	dimensionless spatial coordinate inside the crystallites [–]

be inert and hence, their separation power should be based on size or shape discrimination.

A possible candidate is all-silica Deca-Dodecasil 3 Rhombohedral (DD3R), a clathrasil, firstly synthesized by Gies [16]. The structure of DD3R consists of window-connected cages, in contrast to zeolite frameworks, which makes this material a member of the group of clathrasils. Fig. 1 shows the three types of fundamental cages building up the rhombohedral structure. The crystal structure is built by corner-sharing SiO_4 tetrahedra that are connected to pseudohexagonal layers of face-sharing pentagonal dodecahedra (5^{12} cages). These layers are stacked in an *ABCABC* sequence and are interconnected by additional SiO_4 tetrahedra that form six-membered rings between the layers. Thus, two new types of cages arise, a small decahedron, $4^3 5^6 6^1$ cage, and a large 19-hedron, $4^3 5^{12} 6^1 8^3$ cage. By connecting the 19-hedra cavities through a single 8-ring with an aperture of 4.4 × 3.6 Å, a two-dimensional channel system is formed, which is accessible to small molecules after thermal treatment at 773 K [17]. Up to now, just a few publications deal with the difficult and long (up to 24 days) synthesis and characterization of DD3R [18,19]. Presumably this is related to the tendency of the poorly soluble template (1-adamantanamine) to segregate from the synthesis mixture, yielding to the formation of undesired by-products such as DOH [20] or SGT [21].

The selective adsorption of propylene over propane and *trans*-2-butene and butadiene from other butane and butene isomers on the all-silica DD3R was firstly reported by our group some years ago by studying single component adsorption using a tapered element oscillating microbalance (TEOM) [22]. Later on, Olson et al. [23] studied the sorption properties of some 8-ring zeolites, among them ZSM-58 (DDR structure type), in which the high selectivity for propylene was also inferred from single component adsorption. Propane hardly adsorbs in the chathrasil because its kinetic diameter is larger than the 8-membered ring windows of DD3R.

In this paper we report a considerably accelerated synthesis of DD3R and its performance in the separation of propylene from propane by breakthrough experiments in an adsorption column. An engineering model is presented to describe the breakthrough profiles based on complementary single adsorption experiments, and to estimate diffusion coefficients. This work represents, to the best of our knowledge, the first propane/propylene mixture breakthrough experiments reported for DD3R.

2. Experimental

DD3R zeolite crystals were initially prepared by the method described elsewhere [20]. The synthesis mixture molar ratio of 1-adamantane amine: silica: ethylenediamine: water = 47:100: 404:11240 was prepared as follows. 1-Adamantane amine (Sigma Aldrich, 97%) was dissolved in ethylenediamine (Sigma Aldrich, ⩾99%) and water was then added rapidly. Although different silica sources were investigated (see Table 1), if not specified, Aerosil-200 was the used one. The mixture was placed in a shaking machine for 1 h. After heating to 368 K for 1 h while stirring, the mixture was cooled down in ice and the silica source was then added drop by drop while being stirred vigorously. The mixture was again heated to 368 K in an open vessel while stirring until the solution became clear (the solution changed from white to almost transparent). The first synthesis was performed at 433 K for 25 days under rotatory conditions (60 rpm) [18]. Using the as-synthesised DD3R crystals as seeds in the later syntheses, time could be reduced from 25 to 2 days under the same operating conditions.

A micromeritics ASAP 2010 gas adsorption analyser (stainless steel version) was used to measure the adsorption isotherms of propane and propylene on DD3R at 318, 358 and 383 K, in the pressure range from 0.002 to 120 kPa. These temperatures were considered as representative for the operation range of a commercial