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Zeolite Rho: Highly selective adsorbent for CO2/CH4 separation induced by an structural phase modification

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Zeolite Rho is able to successfully separate CO_2 from CH_4 with the highest selectivity ever observed on the basis of pore diameter and surface polarity. The adsorption of CO_2 provokes structural changes in the zeolite Rho.

Molecular sieves and zeolites are becoming important materials for gas separations and catalysis on the bases of pore aperture and chemical composition, allowing highly selective separations.[1-18] One of the most attractive processes is the separation of CO_2 from CH_4 which constitutes one of the major contaminants of natural gas.[19] The actual technology for the removal of CO_2 from CH_4 is based on aqueous amine scrubbing which involves an energy demanding regeneration process and produces corrosion in the equipments.[19] Therefore, adsorption technologies, such as Pressure Swing Adsorption (PSA), are being studied for this particular application. In this process, one of the components of the gas mixture (CO_2) is selectively adsorbed on an adsorbent at moderate to high pressures and released upon decreasing pressure. Such type of process requires robust adsorbents with high thermal and hydrothermal stability, while resistant to sulfur compounds and slightly acidic media (i.e. processes lifetimes > 10 years are common).[20]

Zeolites can accomplish those properties and their use in CO_2/CH_4 separations is based on the preferential adsorption of CO_2 over CH_4 in the polar cavities and channels of relatively aluminium rich zeolites, such as zeolite 13X, Y (FAU) and A (LTA).[21-26] However, the high affinity of low Si/Al ratio zeolites for CO_2 hinders its desorption. Then, recently it has been found that for LTA zeolites the optimum Si/Al ratio for CO_2 adsorption/desorption cycles is in the range 5-15.[27]

The selectivity for CO_2/CH_4 separation processes with zeolites can be further improved through the fine tuning of their structural pore diameter. In the particular case of CO_2 and CH_4, the kinetic diameters of the two molecules are 3.30 and 3.82 Å,[28] respectively and, therefore, zeolites with pore aperture in between those dimensions, having large adsorption capacity and the adequate polar character could be good candidates for this separation process. One of the zeolites that, in principle, fulfils all these requirements is zeolite Rho. Indeed, this zeolite presents the most adequate polarity (Si/Al close to 5), very high pore volume (0.26 cm^3/g) with a pore diameter (3.6 Å) just in between the kinetic diameters of CO_2 and CH_4[29,30] and has been proposed for O_2/N_2 separation.[31] In this work, we will show the outstanding behaviour of zeolite Rho for performing the CO_2/CH_4 separation.

One zeolite Rho sample having a Si/Al ratio of 4.5 (Table S1) and an averaged crystallite size of 1.5µm was synthesized following a synthesis procedure based on that previously reported.[30] Further synthesis and characterization details are given as Supplementary Information.

This zeolite Rho was employed as adsorbent for CO_2 and CH_4 and the adsorption isotherms were carried out in an IGA-3 gravimetric analyser (Hiden Isochema) equipped with a high pressure transducer. Experimental details of adsorption data collection for building up the corresponding isotherms and data analysis are given as Supplementary Information.

The CO_2 and CH_4 adsorption results obtained on zeolite Rho are shown in Figure 1a, where it is clearly evidenced that CO_2 is adsorbed in a much larger amount than CH_4, yielding very high CO_2/CH_4 equilibrium selectivity factors (α). This parameter is calculated as $\alpha = (Q_{CO2})/(Q_{CH4})$, where (Q_{CO2}) and (Q_{CH4}) are the equilibrium molar uptakes of CO_2 and CH_4 at a given pressure taken from the corresponding single component isotherms. The α factor is plotted against pressure in Figure 1b, where selectivities as high as 10 are obtained at pressure ranges of 400–600 kPa which is a typical pressure for performing the adsorption step in a PSA process.[19] The CO_2/CH_4 selectivity obtained for zeolite Rho is the highest value ever reported for zeolites in this industrially relevant separation, which typically gives values between 1.8 to 3.[23,32,33] A much broader comparison can be done at lower pressure (100 kPa) as it is shown in Table S5. There, it is seen that the α factor of zeolite Rho is 75, while other zeolites do not reach 12 (i.e. the separation is at least 6 times better for zeolite Rho than for any other zeolite).

A convenient procedure for PSA process based on CO_2 adsorption requires that the adsorption takes place at moderate pressures above atmospheric pressure (400–600 kPa) and desorption should be performed, preferentially, at atmospheric pressure (to avoid vacuum and/or heating operations).[19] Consequently, the CO_2 working capacity parameter can be defined as the difference of the uptake at 600 kPa minus the uptake at atmospheric pressure, which are directly calculated from the isotherms (Fig. 1a) giving a result of 2.2 mmol/g, which is a good value for zeolites, being close to the best LTA adsorbent.[27] Another important parameter to be considered when using zeolites in this separation process is the regenerability of the adsorbent. This can be defined as the ratio between the working capacity and the uptake at the adsorption pressure (600 kPa) expressed as percentage. In the case of zeolite Rho, the regenerability calculated in this

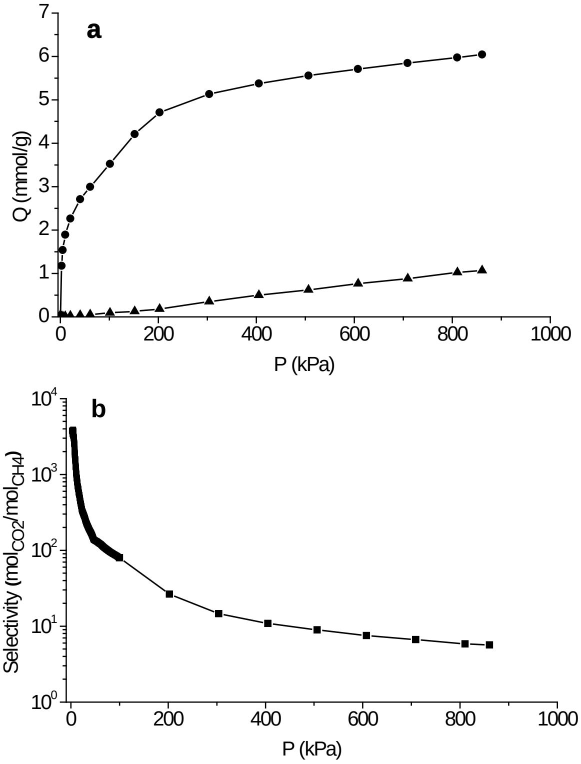

Fig. 1 CO_2 (●) and CH_4 (▲) adsorption isotherms of zeolite Rho at 303 K (a), and CO_2/CH_4 equilibrium selectivity factor according to volumetric and gravimetric measurements (b).

manner gives a value around 40% which is acceptable.

Another way to estimate the regenerability of an adsorbent is the determination of the energy released during the adsorption process, by means of the isosteric heat of adsorption (q_{st}). To do that, high resolution isotherms at low pressures and different temperatures were collected, being coincident in the common range to those obtained at high pressures (see Supplementary Information). The isoteric heat of CO_2 adsorption plot shows (figure S4) a smooth decrease of the energy with the CO_2 loading (from 33 to 24 kJ/mol). Attempts to calculate the isosteric heat from the CH_4 adsorption have failed because the equilibrium is not reached at any temperature and pressure (see Supplementary Information), indicating that CH_4 does not penetrate inside the pores of zeolite Rho in significant amounts. The lack of adsorption of CH_4 was confirmed by calorimetric adsorption measurements performed on a Sensys-Evo Calorimeter from Setaram equipped with a thermogravimetric accessory. The heat of adsorption of CH_4 at 100 kPa and 303 K was nearly zero, within the experimental error, while the heat of adsorption of CO_2 under equal conditions was 33.9 kJ/mol, in good agreement with the calculated value by applying the Clausius-Clapeyron equation to the CO_2 isotherms (Fig. S4).

This CO_2 adsorption behaviour for zeolite Rho is similar to that obtained for the LTA zeolite with a Si/Al ratio of 5,[27] indicating a similar adsorption and regenerability performance as a consequence of the analogous polar character and composition, but with the additional benefit in the case of zeolite Rho, of a much higher CO_2/CH_4 selectivity.

Then, from these results it seems feasible that zeolite Rho could be a useful adsorbent for performing CH_4 purification from natural gas. In order to confirm this, we have determined the breakthrough curves for separation of a CO_2/CH_4 mixture in a fixed bed continuous separation system. The corresponding curves displayed in Figure 2 show that CO_2 is preferentially retained while CH_4 passes with practically no retention on the adsorbent bed allowing an excellent separation.

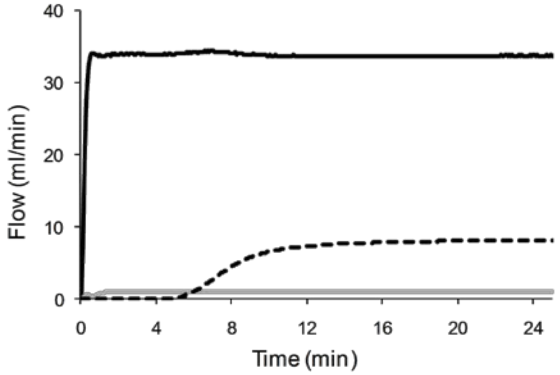

Fig. 2 Breakthrough curves corresponding to the separation of a CO_2/CH_4 gas mixture on zeolite Rho containing 80% CH_4 and 20% CO_2 run at 303 K and 100 kPa, using 2.5 ml of zeolite Rho and GHSV = 1000 h^{-1}. Solid black line is CH_4, dash black line is CO_2, and gray line is He (internal standard).

Therefore, we have shown that zeolite Rho is able to perform the separation of CO_2 from CH_4 with very high selectivity taking benefit of the diameter of its pore aperture, which lies in between those of both molecules. Zeolite Rho is characterized by a large CO_2 adsorption capacity and the appropriated polar character for allowing the regeneration of the adsorbent. Also, it exhibits an extremely high selectivity for natural gas purification process which is particularly useful when the amount of CO_2 to be removed is small.

The observed high selectivity for CO_2 on zeolite Rho could be explained just considering its pore aperture (3.6 Å). However, other zeolites such as SAPO-34 (IZA code: CHA; pore aperture 3.8 Å) or Deca-dodecasil 3R (IZA code: DDR; pore aperture 3.6 x 4.4 Å) show much lower selectivities[26,32,34,35] (see also Table S5), even though their pore apertures lie in between kinetic diameters of CO_2 and methane. Then, we have studied the structural modifications of zeolite Rho during the course of the CO_2 adsorption process by using high pressure 'in-situ' X-Ray diffraction technique (see Supplementary Information for experimental and refinement details). It has been found that severe modification of the zeolite Rho structure occurs upon CO_2 adsorption. Indeed, the structure of zeolite Rho prior to CO_2 adsorption (i.e. calcined at high temperature and kept under N_2) was refined in the space group *I*-43*m*, being very similar to that described for dehydrated zeolite Rho, in which the nearly circular pores are distorted into more elongated ones.[36,37] This results in a effective pore aperture for dehydrated zeolite Rho of 2.9 x 6.0 Å, according to the Rietveld Refinement. This structure is stable up to 100 kPa of

CO_2. At 200 kPa of CO_2, there is a slow phase transition from *I*-43*m* to *Im*-3*m* as evidenced by the appearance of new X-Ray diffraction peaks and the corresponding decrease of the intensities of the characteristic X-Ray peaks corresponding to the *I*-43*m* phase (Figure 3).

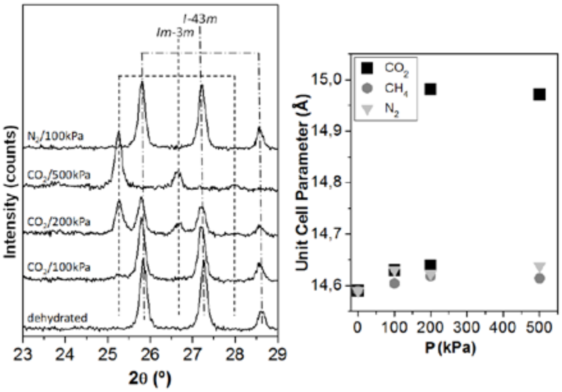

Fig. 3 Left. Fragment of X-Ray diffraction patterns of zeolite Rho submitted to diverse CO_2 pressures. Right. Cubic unit cell paremeters of zeolite Rho submitted to different pressures of CO_2, CH_4 and N_2.

Further increase of the CO_2 pressure ends up the phase transition, resulting in the pure *Im*-3*m* zeolite Rho with a nearly circular pore of 4.0 Å. This pahse tranasition is fully reversible and just by fluxing N_2 through the sample, the I-43m structure is recovered (Figure 3, Left). Similar experiments carried out using CH_4 or N_2 instead of CO_2 do not show any change of the *I*-43*m* symmetry or the unit cell parameters, remaining the same pore aperture of 2.9 x 6.0 Å even at 500 kPa (Figure 3, Right). Then, it is possible to conclude that the structural modification of zeolite Rho is not due to the applied pressure, but is mostly due to the filling of the empty space of the zeolite. This is further supported by the presence of an odd feature in the CO_2 adsorption isotherm in between 100 and 200 kPa (see Figure 1a), corresponding to the observed phase transition.

Tentatively, we propose that the extreme high selectivity and very high CO_2 adsorption capacity of zeolite Rho is mainly due to a combination of the pore aperture and the expansion of the void volume upon phase transition, resulting in the most selective zeolite ever described for CO_2/CH_4 separation (see Table S5 for comparing to available data in the literature).

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization of zeolite Rho, and further CO_2 and CH_4 adsorption and X-Ray diffraction results. See DOI: 10.1039/b000000x/

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