Encapsulation of hydrogen in cadmium-exchanged zeolite rho; temperature-programmed diffusion studies

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Cadmium-exchanged zeolite rho encapsulates 161 μmol g^{-1} of hydrogen at 100 °C and 620 μmol g^{-1} at 200 °C, (in 2 h and at 1 atm), the highest ever observed for any zeolite at 1 atm; hydrogen-exchanged zeolite rho, however, shows negligible uptake of hydrogen, providing evidence that the cadmium ion is directly responsible for hydrogen encapsulation.

Encapsulation studies of non-polar gases *e.g.* hydrogen, argon, xenon *etc.*[1–11] have been done in order to understand the process of intracrystalline diffusion in zeolites. The diffusive transport is an activated process.[1–7] Therefore, these molecules are interesting probes in the characterization of available sites for encapsulation (or entrapment). Hydrogen is of particular interest, since it is the most mobile, due to its small size. The commercial development of storage media for hydrogen is another objective. Zeolites, when ion-exchanged suitably, can entrap non-polar gases in the cavities and therefore have been considered as possible alternatives to metal hydrides for hydrogen storage.[1,8] Ion-exchanging zeolites with large cations *e.g.* Cs^+, Eu^{3+}, Rb^+, *etc.*[4,5] results in selective blocking of openings leading to the zeolitic cages. By increasing the temperature, it is possible to impart greater vibrational energy to the heavy cations and allow the gas to enter the cages. Cooling the material results in entrapment of the gas inside the cage.

Our research involves the study of the encapsulation properties of Cd/Cs-rho zeolite[12,13] ($Na_{0.02}Cs_{1.87}Cd_{5.05}Si_{36}Al_{12}O_{96}$) by temperature-programmed diffusion (TPDi). We report here, the encapsulation uptakes of hydrogen on Cd/Cs-rho at 100 and 200 °C at different times of encapsulation. The encapsulation experiments were performed in a continuous flow reactor with an empty volume of 1.5 cm^3 using 30 mg of pelletized catalyst (about 1 mm in diameter). Pure hydrogen was fed into the reactor for the desired time and at the desired temperature. The reactor was then cooled rapidly to room temperature still under hydrogen flow. The TPDi experiment was then carried out after switching the gas to argon. The on-line analysis was done with a mass spectrometer (NUCLIDE 12-90-G).

Preliminary experiments performed at 50 °C show an increase in encapsulation uptake from 71 μmol g^{-1} to 85 μmol g^{-1} upon increasing the time of encapsulation from 2 to 4 h. The peak also exhibits a shift from 90 to 102 °C in this process. This trend has been observed before by Efstathiou *et al.*[4,5] in zeolites A and X. The peak migration to higher temperatures with increase in uptake is exactly opposite to what is observed in the case of temperature programmed desorption (chemisorption).[14] The processes here, therefore, are due to encapsulation and diffusion. The uptakes for zeolite rho are about 30 times higher than that of NaX and NaA[4,5] (less than 2 μmol g^{-1}) under the same conditions of temperature and pressure.

Experimental results at 100 °C are shown in Fig. 1. An increase in uptake with time of encapsulation is observed. A second peak at > 200 °C, emerges, notwithstanding the approximate saturation of the first site (about 110 °C). The increase in uptake from 161 μmol g^{-1} (2 h) to 213 μmol g^{-1} (4 h) to 263 μmol g^{-1} (6 h) with increase in time confirms the fact that given more time, the opportunity for diffusion is enhanced, thereby causing more uptake. The first peak has been observed to reach a certain level and with further increase in time, the other peaks seem to emerge slowly. Upon increasing the temperature of encapsulation (50 to 100 °C), the access to more energetic sites is enhanced, due to intracrystalline diffusive transport being the rate-controlling step. The hydrogen is removed from these sites at about 220–250 °C under our experimental conditions.

Encapsulation experiments at 200 °C for 2 h show hydrogen uptakes of 620 μmol g^{-1}, much higher than the available data for zeolites A, Sigma-1, ZK-5, sodalite and other forms of zeolite rho.[8–10] TPDi results indicate 3 distinct peaks at 107, 295 and 345 °C. A slight hump at 450 °C in the data (Fig. 2) could possibly indicate the presence of another site but this cannot be concluded as yet. Further encapsulation experiments done over periods of 1 h and 0.5 h, show a redistribution of intensity, with the second and third peaks decreasing in intensity and the first increasing in intensity with decreased time of encapsulation. Fig. 2 shows comparative data for the three spectra. The higher temperature caused very large increments in the encapsulation of hydrogen. The total uptake is almost 8 times larger than that observed at 50 °C. Note that the intensity of the first peak of the 200 °C experiment has dropped in comparison to the results for

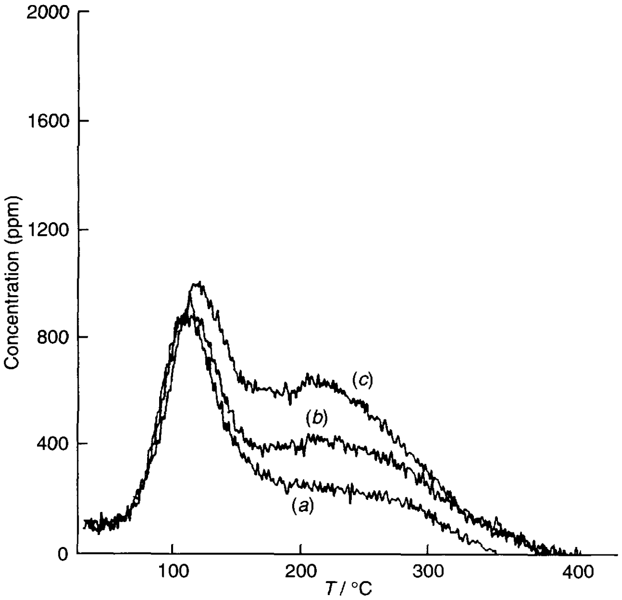

Fig. 1 TPDi spectra: hydrogen encapsulation temperature = 100 °C, heating rate = 24 °C min^{-1}; encapsulation time = 2 (*a*), 4 (*b*) or 6 h (*c*)

100 °C, for the case of 2 h encapsulation. The second and third peaks are extremely intense which shows that at a higher temperature, *i.e.* 200 °C, the vibrational energy of the cations (particularly cadmium) increases causing the hydrogen to enter into the sites of higher activation energy. A change in the vibrational energy is expected to alter the rate of hydrogen diffusion since this is an activated process. An increase in the vibrational energy of cations can lead to the displacement of the cation and subsequent room for diffusion of hydrogen through the eight-ring window. By decreasing the time of the encapsulation to 1 h and then to 0.5 h, peak 1 periodically increases and peaks 2 and 3 are decreased. This probably indicates in the beginning, that hydrogen has a tendency to fill the site having the lowest energy. It then fills the higher energetic sites. At a higher time of encapsulation, there could be a migration of encapsulated hydrogen from the lower to the higher energy sites (Fig. 2). At smaller times of encapsulation (0.5 and 1 h) the redistribution of the encapsulated hydrogen may occur to a lesser extent. The uptakes at 1 and 0.5 h are 525 μmol g^{-1} and 520 μmol g^{-1}, respectively. No such redistribution occurs at the 100 °C experiments because at those conditions the number of available sites is much smaller.

Encapsulation experiments done on zeolite H-rho at 100 and 200 °C reveal no uptake at all. This bears interesting contrast to Cd/Cs-rho which has very high uptakes. Cd/Cs-rho has 5.05 cadmium ions and 1.87 caesium ions per unit cell. It is therefore likely that either the cadmium ions (1.03 Å) or the caesium ions (1.65 Å) or both have a strong role in the hydrogen encapsulation process.

In conclusion, one of the most interesting observations for encapsulation of hydrogen in Cd/Cs-rho is the large hydrogen uptake even at pressures of 1 atm. Hydrogen encapsulation of this magnitude has not been observed for any other zeolitic system. The cadmium cation has a very strong effect upon the entrapment of hydrogen and this is supported by experiments showing no encapsulation of hydrogen in H-rho zeolite (which contains only 0.93 caesium ions per unit cell). The consistent appearance of more than one site of encapsulation indicates that the cation might be positioned near the windows or the channels connecting the cages. This hinders the transport of hydrogen into the 'cavities' or 'sites', where they can be entrapped. It is not possible to conclude with finality the positions of the cadmium ions or the caesium ions, from mere encapsulation experiments, but the encapsulation trends are indicative of there being an energy distribution which may be closely related to electric fields of the cations in the unit cell.

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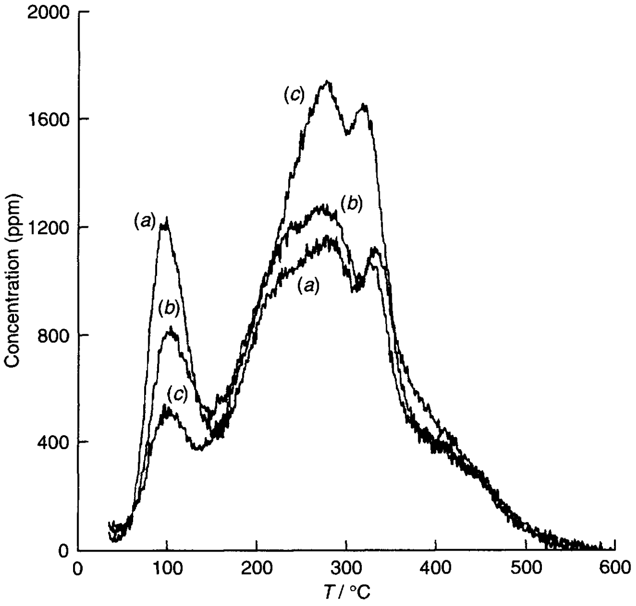

Fig. 2 TPDi spectra: hydrogen encapsulation temperature = 200 °C, heating rate = 24 °C min^{-1}; encapsulation time = 0.5 (*a*), 1 (*b*) or 2 h (*c*)

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