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Encapsulation studies of hydrogen on cadmium exchanged zeolite rho at atmospheric pressure

Venkatesan V. Krishnan [a], Steven L. Suib [a,b,c,*], David R. Corbin* [d], Stephan Schwarz [d], Glover E. Jones [d]

[a] Department of Chemical Engineering, U-222, The University of Connecticut, Storrs, CT 06269, USA
[b] Department of Chemistry, U-60, The University of Connecticut, Storrs, CT 06269, USA
[c] Institute of Material Science, The University of Connecticut, Storrs, C T06269, USA
[d] Central Research and Development, DuPont Company Experimental Station, P.O. Box 80262, Wilmington, DE 19880-0262, USA

Abstract

Temperature programmed diffusion (TPDi) has been used to study the encapsulation of hydrogen in cadmium exchanged Cs-rho zeolite. The amount encapsulated after 2 h has been observed to be about 71 μmol/g at 50°C and 1 atm. This amount is over 30 times the amount of hydrogen encapsulated with NaX or NaA at 37°C for the same time and pressure. Upon increasing the encapsulation temperature to 100°C, the amount encapsulated increased to 161 μmol/g (2 h of encapsulation). At 200°C, the encapsulate is about 620 μmol/g, for the same pressure and time. With increasing temperature, more than one peak is seen in the TPDi spectra, revealing the availability of more than one site [1] for the encapsulation. 3 peaks are observed in TPDi spectra for the encapsulation at 200°C – at 107, 295 and 345°C. Large encapsulated amounts of hydrogen arise from blocking effects caused by the presence of cations (cadmium and/or cesium). Experiments for encapsulation of hydrogen on H-rho (hydrogen exchanged zeolite rho) show negligible uptake of hydrogen, proving that the presence of either the cadmium ion (5.05 Cd^{2+} per unit cell) or the cesium ion (1.87 Cs^{+} per unit cell) or both is directly responsible for the encapsulation of hydrogen.

For encapsulation at 200°C, possible migration of the encapsulate among the sites seems to occur with encapsulation time. This could explain the relative changes in the intensities of the 3 peaks in the TPDi spectra for the encapsulation at 200°C.

Keywords: Encapsulation studies; Hydrogen; Cadmium exchanged zeolite rho; Zeolite

1. Introduction

A potential application of materials that encapsulate gases is the development of storage media for hydrogen and other gases. With their cage and channel structure as well as their ion-exchange capacity, molecular sieves offer enormous potential for encapsulation of non-polar gases.

Studies of encapsulation of non-polar gases such as hydrogen, argon, xenon, etc. [1–7,14,17,18] with zeolites are useful from a fundamental point of view, because these molecules have small adsorptive interactions with the zeolite framework. The mobility of the gases in the

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* Corresponding authors.

[1] The word "site" denotes a cavity or a cage or maybe even a prism or any enclosure which could entrap hydrogen.

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zeolitic framework is controlled by diffusive transport. The diffusive transport is essentially activated in its mechanism, with an Arrhenius dependence on temperature [1–7]. Therefore, these molecules are interesting probes in the determination of available sites for encapsulation. Hydrogen is of particular interest, since it is most mobile, due to its small size. By ion-exchanging different zeolites with large cations, e.g. Cs^+, Eu^{3+}, Rb^+, etc. [1,4,5,14,16,17], in varying amounts, selective blocking of channels and windows in the zeolitic framework can be achieved [18].

Structural properties of zeolite-rho have been investigated by X-ray powder [13] and neutron diffraction techniques [8–10,12]. Studies of the variation of crystal structure with temperature have also been done [8–10,13]. The primary structural difference in zeolite-rho in comparison with A is that the former is a 3-dimensional network of alpha-cages (cubo-octahedra), which are connected to each other by octagonal prisms whereas in the latter case, beta (sodalite) cages are connected to each other by cubic prisms. Zeolite-rho therefore looks like a body centered cubic structure of alpha cages [8]. Recent relevant structural data from the work of Parise et al., for Cd-rho zeolite ($Na_{0.06}Cs_{0.22}Cd_{4.8}Si_{37}Al_{11}O_{96}$), show the behavior of unit cell dimensions and symmetry of these materials as a function of hydration and temperature [13]. The enormous structural flexibility reported in the above reference does not extend to the Cd/Cs-rho studied in this paper ($Na_{0.02}Cs_{1.87}Cd_{5.05}Si_{36}Al_{12}O_{96}$), which has about 1.65 cesium ions more than the sample studied by Parise et al. [13].

Coupling of the techniques of encapsulation and temperature programmed diffusion (TPDi) is designed to illustrate a simple method for examining the role of cations present in exchange sites of zeolite-rho. This could have a

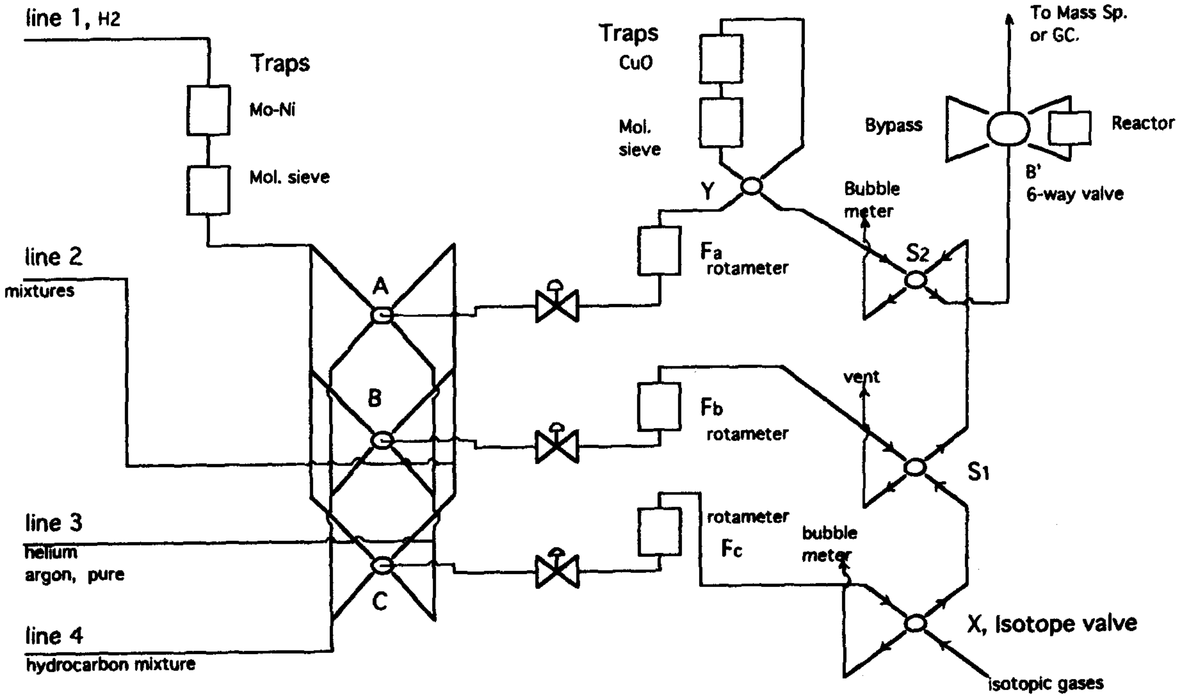

Fig. 1. Panel flowsheet.

bearing on shape selectivity in reactions of heavier molecules (hydrocarbons), depending upon the sizes of cations and reactant molecules.

2. Experimental section

All experiments were done in a stainless steel microreactor with an empty volume of 1.5 cm^3. The Cd/Cs-rho powder was made into pellets of approximately 1 mm in diameter. About 30 mg of catalyst was spread suitably to minimize the aspect ratio (axial length/diameter) of the bed. The small volume of the reactor and minimal depth of the bed are optimal conditions for doing temperature programming experiments because of the absence of axial gradients in temperature and concentration.

The exit stream from the reactor goes into the inlet of a mass spectrometer (NUCLIDE 12-90-G), where the pressure was carefully maintained by an inlet pump and an inlet valve. The signal (hydrogen in this case) was measured by an electron multiplier and recorded by the data acquisition system. The schematic for the panel is shown in Fig. 1.

The synthesis of Cd/Cs-rho zeolite is carried out by ion-exchange of the Na/Cs-rho ($Na_{6.7}Cs_{3.0}Si_{36.3}Al_{11.7}O_{96}$) six times with a 10% $NaNO_3$ solution (by weight) at 90°C for 1 h. The starting Na/Cs-rho material has been prepared by a modified procedure of Robson's patent [11]. After the exchange with the $NaNO_3$ solution, the resultant solution was exchanged six times with 10% Cd $(NO_3)_2$ at 90°C for 1 h. The formula of the final form of Cd/Cs-rho is as follows – $Na_{0.02}Cs_{1.87}Cd_{5.05}Si_{36}Al_{12}O_{96}$. Separation of solids and liquids between exchanges was achieved by centrifugation.

Pre-treatment of the Cd/Cs-rho materials is an essential part of the procedure prior to the encapsulation. The pre-treatment involves the complete removal of moisture from the zeolite framework. In order to achieve this, the sample was outgassed on a vacuum line and heated simultaneously in steps of 50°C. The pressure was carefully monitored after every step change of 50°C. No further change in temperature was effected until the pressure stabilized at the lowest possible value. This procedure was repeated until the final temperature reached 400°C. The sample was outgassed at this temperature for about 3 days at a pressure of 6.6×10^{-4} N/m^2, before being transferred to the reactor under inert conditions. The sample was further heated on-line in argon to 400°C until the water signal reached a minimum in the mass spectrometer. To ensure that the signal is indeed a minimum, the inert argon gas was routed through a bypass and the water signal was measured and compared with the stream coming from the reactor.

The hydrogen gas was encapsulated at 50, 100, 125, 150 and 200°C over periods of 1, 2, 4 or even 6 h for different experiments. The catalyst was cooled down to room temperature while still under a hydrogen stream. The gas stream

Table 1
Encapsulation uptakes of hydrogen at various times and temperatures: zeolite Cd/Cs-rho

T (°C)	Time (h)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)	Ramp (°C/min)	Amount (μmol/g)
50	2	90			18	71
50	2	100			24	70
50	4	102			18	85
50	6	101			18	88
100	2	109			24	161
100	4	112	213		24	213
100	6	120	215		24	263
200	0.5	106	286	343	24	519
200	1	107	280	341	24	526
200	2	107	298	340	24	616

was then switched to argon at room temperature and flushed for 15 min to remove weakly held hydrogen. The sample was then heated from 30 to about 400°C or 550°C using heating rates of 18 and 24°C/min. Both the hydrogen and the argon gas flow rates were 30 cm^3/min. A flow rate of 30 cm^3/min with a heating rate of 24°C/min gave a very good deconvoluted set of peaks (as shown in the results), with appreciable intensity.

3. Results

Table 1 summarizes the results for the encapsulation uptakes for the hydrogen at different temperatures and times. The temperature of encapsulation (°C), time for encapsulation (h), location of desorption peaks (°C), ramp rate (°C/min) and amounts of hydrogen (μmol/g) encapsulated are all shown in Table 1.

An error of about 5°C is likely in the measurement of the peak temperatures in the TPDi spectra. Based on studies of reproducibility for encapsulation at 200°C, there appears to be an error of about 6% in the estimation of the amount encapsulated.

Figs. 2–4 show the temperature programmed diffusion (TPDi) spectra as measured by mass spectrometry. Preliminary experiments done at 50°C (Fig. 2) show an increase in encapsulation uptake from 71 to 85 μmol/g upon increasing the time of encapsulation from 2 to 4 h. The peak also exhibits a shift from 90 to 102°C as the time of encapsulation is increased from 2 to 4 h. This trend has been observed before by Efstathiou et al. [4,5] in zeolites X and A. The encapsulation uptake after 6 h approaches 88 μmol/g indicating, perhaps, a saturation value for this temperature. Fig. 2 shows the decapsulation as a function of temperature. Increasing the heating rate from 18 to 24°C/min, keeping the time of encapsulation fixed at 2 h, yields 70 μmol/g of uptake, in agreement with the amount for 18°C/min. This result provides a check for the reproducibility of the experiment.

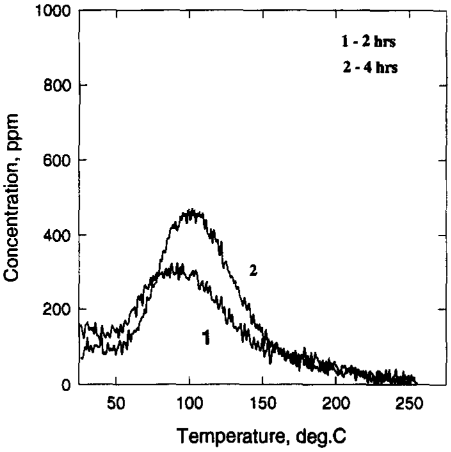

Fig. 2. TPDi spectra: hydrogen encapsulation temperature = 50°C; heating rate = 18°C/min.

Experiments carried out at 50°C show a substantial increase in encapsulation uptake as compared to those for NaX and NaA [4,5]. NaA encapsulates about 1.13 μmol/g of hydrogen at 37°C [5] and about 2 μmol/g at 100°C after 2 h. NaX encapsulates about 1.64 μmol/g of hydrogen at 37°C in 2 h [4]. These comparative figures give an indication of the phenomenal increase in the encapsulation of hydrogen in the Cd/Cs-rho zeolite material as compared to the X and A zeolites. Encapsulation effects are strongly dependent on the presence of cations in the framework. It is therefore a good idea to provide more energy to the cations (increased thermal vibrations) in the framework by increasing the temperature. This enhances the access of gas molecules into several cages in the zeolite framework which may be inaccessible at lower temperatures.

Experiments have been carried out at 100°C as shown in Fig. 3. A heating rate of about 24°C/min was found to be optimal in giving peaks of good intensity coupled with deconvolution of broad peaks. Therefore, a heating rate of 24°C/min has been used in most cases to collect TPDi spectra. Fig. 3 shows the increase in uptake with respect to time of encapsulation. It also shows the emergence of a second peak above 200°C, notwithstanding the approximate

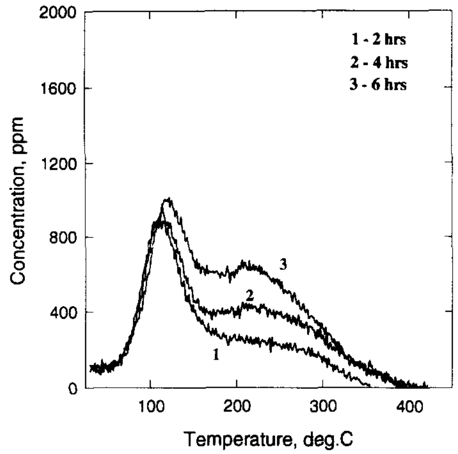

Fig. 3. TPDi spectra: hydrogen encapsulation temperature = 100°C; heating rate = 24°C/min.

saturation of the first site (about 110°C). This observation is typical of a diffusion controlled encapsulation process, wherein gradual availability of more energetic sites occurs with increase in the temperature of encapsulation. The amounts encapsulated are shown in Table 1.

Encapsulation experiments at 200°C show 3 distinct peaks at 107, 295 and 345°C. A slight hump at 450°C in the spectra (Fig. 4) could possibly indicate the presence of another site but cannot be concluded as yet. Moreover, the encapsulation uptake has increased enormously to over 600 μmol/g. This situation shows a decrease in the amount occupying the first site at 107°C in comparison to the encapsulation at 100°C for a period of 2 hours. Further encapsulation experiments done over a period of 1 and 0.5 h, show a redistribution of intensity, with the second and third peaks decreasing in intensity and the first, going up in intensity with decreased time of encapsulation. Fig. 4 shows a comparative picture of the 3 spectra. The uptakes observed in this work have been compared with the encapsulation results in other systems done by various researchers and listed in Table 2. Our data are at atmospheric pressure and, therefore, show very high uptakes in comparison to these other materials.

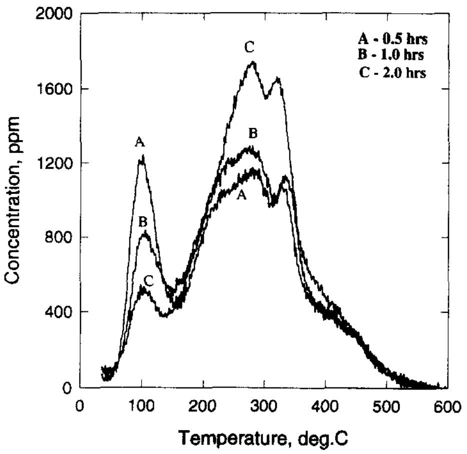

Fig. 4. TPDi spectra: hydrogen encapsulation temperature = 200°C; heating rate = 24°C/min.

Table 2
Comparison of hydrogen uptake on zeolite Cd/Cs rho with other microporous materials

Reference	T (°C)	Pressure (atm)	Amount (μmol/g)	Material
[17]	350	153	200	NaA
[18]	350	129	871	$Cs_{2.5}$ NaA
[1]	300	905	3000	$Cs_{5.4}$ NaA
This study	200	1	620	Cd/Cs rho
This study	200	1	0	H-rho
[19]	300	100	400	Sodalite

Encapsulation experiments done on zeolite H-rho at 100 and 200°C show that no uptake occurs at all. This bears interesting contrast with Cd/Cs-rho which has very high uptakes. Such observations will be discussed below.

4. Discussion

The experimental results for encapsulation at 50°C show only one peak, indicating the presence of one available site for encapsulation. At an encapsulation temperature of 100°C, the vibrational energy of the cations has been enhanced, thereby allowing access into sites of higher energy. The increase in uptake with increase in time (Fig. 3) confirms the fact that given more time, the opportunity for diffusion is enhanced and, therefore, there is more uptake.

The trends obtained in the TPDi spectra clearly show an increase in uptake (in comparison to Fig. 2) as shown in Fig. 3. The first peak has been observed to reach a certain level and with further increase in time, the other peaks emerge slowly. At higher times, the access to more energetic sites is enhanced, in light of intracrystalline diffusive transport being the rate controlling step.

The low energetic site has a temperature maximum of about 108–110°C. The sites of higher energy slowly appear at temperatures greater than 225°C (Table 1). All cages in the Cd/Cs-rho are alike and, therefore, the differences in encapsulation sites are not large. The Cd/Cs-rho material just has the alpha-cubo-octahedral cage and the octahedral prism window which connects each such cage unlike NaA and NaX zeolites, where there is a distinct difference between the sodalite cage and the supercages. The encapsulation mechanism is, therefore, expected to be more dependent upon the local positioning of some of the cadmium ions and/or the cesium ions.

Fig. 4 shows the results of encapsulation at 200°C. The reproducibility was nearly flawless (checked over a set of 4 experiments). The middle peak seems to have migrated to 290–295°C, while the first and the third peak remain at 107 and 345°C, respectively. The higher temperature caused very large increments in the encapsulation of hydrogen. The total uptake is almost 4 times that which was observed for 100°C for the same time of 2 h. Note that the intensity of the first peak has dropped in comparison to the results for 100°C, for the case of the 2 h encapsulation. The second and third peaks are extremely intense which shows that given the higher temperature, i.e. 200°C, the vibrational energy of the cations (particularly cadmium) is so high that most of the hydrogen goes to the energetically higher sites. 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 that in the beginning, the hydrogen has a tendency to fill the site with least energy. It then fills the higher energetic sites. It is also possible that at a higher time of encapsulation, there could be a migration of encapsulated hydrogen from the lower to the higher energy sites. Fig. 4 demonstrates this trend clearly. It is suggested that at smaller times of encapsulation (0.5 and 1 h) the redistribution of the encapsulated hydrogen may occur to a lesser extent. From Fig. 4 and Table 1, it is shown that the total uptake still increases with time, although a transfer of intensities from peak 1 to peaks 2 and 3 clearly occurs.

The above results are consistent with activated diffusion. A case may be made for activated chemisorption, but is least likely, for two reasons. Firstly, there are no sites in the zeolite that would induce hydrogen chemisorption. The highest temperature to which the sample has been subjected to hydrogen is only 200°C. At this temperature, it is improbable for the reduction of either cadmium or cesium, thereby eliminating the creation of any sites for hydrogen chemisorption. Secondly, in a chemisorptive process, the peak temperature T_m, obtained from a temperature programmed experiment usually shifts to a lower value, with increase in uptake [15]. This occurs because the heat of desorption decreases with surface coverage [15]. Such behaviour has not been seen in any of our TPDi spectra. The peaks are imprecise, broad and have a tendency to shift to higher values, with higher uptake (Fig. 2). The spectra obtained are therefore more likely to be due to temperature programmed diffusion (TPDi) than temperature programmed desorption (TPD) and the peaks obtained are a measure of the activation energy of diffusion as opposed to heats of sorption.

The total lack of hydrogen uptake in H-rho zeolite at both 100 and 200°C, suggests that the presence of cations is vital to the encapsulation of hydrogen in the system.

5. Conclusions

One of the most interesting observations for encapsulation of hydrogen in Cd/Cs-rho is the large quantity encapsulated in the cages even at pressures of 1 atm. A hydrogen encapsulation of this magnitude has not been observed for any other zeolitic system. The cadmium and the cesium cations seem to have a very strong effect on hydrogen entrapment and this is supported by experiments showing no encapsulation of hydrogen in H-rho zeolite (which contains only 0.93 cesium ions per unit cell). The consistent appearance of 3 sites of encapsulation demonstrates the role of the cation and the importance of cation positions near the windows or the channels connecting the cages. It is not possible to conclude with finality the positions of the cadmium cation from mere encapsulation experiments, but the encapsulation trends are indicative of there being an energy distribution which may be closely related to the electric fields of the cations in the framework. This energy distribution could be related to the activation energy of diffusion.

Finally, it is possible to use small pore materials like zeolite rho as encapsulating media for non-polar gases, by selectively ion exchanging cations such as cesium or cadmium, in varying amounts. By ''designing'', an optimal material we can entrap large quantities of non-polar gases without having to go up to too high a pressure. Subsequent controlled release of gases by a decapsulation process is fundamentally simple and does not require high temperatures as is usually the case with metal hydrides.

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