

Hydrogen storage in ion-exchanged zeolites

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Received 4 June 2004; received in revised form 2 December 2004; accepted 8 December 2004

Available online 2 August 2005

Abstract

The hydrogen storage properties of zeolites X, Y, A and Rho containing various exchangeable cations have been investigated. All hydrogen storage capacities were measured at a temperature of $-196\text{ }^{\circ}\text{C}$ and a pressure range of 0–15 bar, using a constant pressure thermogravimetric analyser. The results show that, zeolites exhibit diverse behaviour with respect to hydrogen uptake, dependent on both the framework structure and the nature of the cations present. A major factor influencing uptake is the available void space: in zeolites A and Rho pore blocking by large extraframework cations is a major factor restricting hydrogen uptake, but in zeolites X and Y, blocking does not occur. This study also suggests that cations may act as binding sites for hydrogen molecules. For zeolites X and Y, hydrogen uptake relates closely to the measured BET surface area. The highest gravimetric storage capacity of 2.19 wt.% was obtained for CaX. Volumetric storage densities of up to 31.0 kg H_2/m^3 (143 H_2 molecules/unit cell) and 30.2 kg H_2/m^3 (144 H_2 molecules/unit cell) were achieved for CaX and KX, respectively.

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Keywords: Zeolites; Ion exchange; Hydrogen storage; Hydrogen adsorption

1. Introduction

Zeolites are a large class of highly crystalline aluminosilicate materials, defined by a network of linked cavities and pores of molecular dimensions that gives rise to their molecular sieving properties [1]. For many decades, they have been used in numerous industrial applications such as the separation of hydrocarbons and the removal of impurities from gas streams [1,2]. With increasing research directed towards finding a suitable solid-state hydrogen storage medium [3], zeolites have recently been considered as potential hydrogen storage materials [4,5]. They are of interest because the diameter of the cages and the channels can be controlled by exploiting their ion-exchange property to modify the valence state and the size of the exchangeable cations. Thus, there can be direct manipulation of the available void space of

the zeolite [6], the chemical nature of possible binding sites and the ease of access of hydrogen molecules to the internal pore space. Previous studies have reported that zeolites can store small amounts of hydrogen (<0.3 wt.%) if loaded at room temperature [4,5,7] or at temperatures $>200\text{ }^{\circ}\text{C}$ [5,7]. At cryogenic temperatures, substantially higher hydrogen storage capacities (>1 wt.%) can be reached [5,8]. In order to examine the role of the framework structure and exchangeable cations in hydrogen adsorption, we report here the results of an investigation of hydrogen storage in zeolites X, Y (both FAU structure type), A (LTA) and Rho (RHO), containing alkali metal cations (Na^+ , K^+ , Rb^+ , Cs^+) and alkaline earth metal cations (Mg^{2+} , Ca^{2+} , Sr^{2+}).

2. Experimental

NaX, NaA and NaCsRho zeolites were synthesized by hydrothermal methods as described elsewhere [5]. NaY is a

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commercial product purchased from Aldrich Chemical Company Inc. NaCsRho was initially ion-exchanged using an aqueous NH_4NO_3 solution. All further ion exchanges on zeolite Rho were then carried out on NH_4Rho . Ion exchange of zeolites X, Y, A and Rho was performed by conventional methods using aqueous nitrate solutions. For the alkali metal cations, 0.1 M aqueous nitrate solution was used. For the alkaline earth metal cations, 0.4 M $\text{Mg}(\text{NO}_3)_2$, 0.4 M $\text{Ca}(\text{NO}_3)_2$ and 0.2 M $\text{Sr}(\text{NO}_3)_2$, solutions were employed. The exchange procedure was repeated two to five times at a specific temperature of 60, 70 or 80 °C.

Powder X-ray diffraction (XRD) patterns obtained on a Siemens D5000 X-ray diffractometer with $\text{Cu K}\alpha_1$ radiation were used for routine characterization of the as-synthesized parent zeolites and ion-exchanged zeolites, in order to confirm phase purity and crystallinity. Scanning electron microscopy (SEM) together with energy dispersive X-ray (EDX) analysis on a JEOL 6300 was used for morphological examination and estimation of the degree of ion exchange. BET surface area measurements were obtained on a Micromeritics ASAP 2010 machine that has a 1000 mmHg transducer, using nitrogen adsorption at -196 °C. The hydrogen storage capacities of the zeolites were determined on a Hiden constant pressure thermogravimetric analyser, known as an Intelligent Gravimetric Analyser (IGA) system. Prior to the hydrogen adsorption measurements, each sample of mass ~ 100 mg was loaded in a glass sample bulb and extensively dehydrated by heating to 400 °C in vacuum. A liquid nitrogen

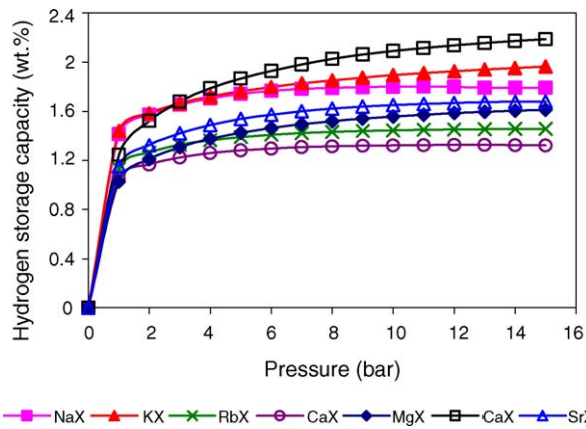
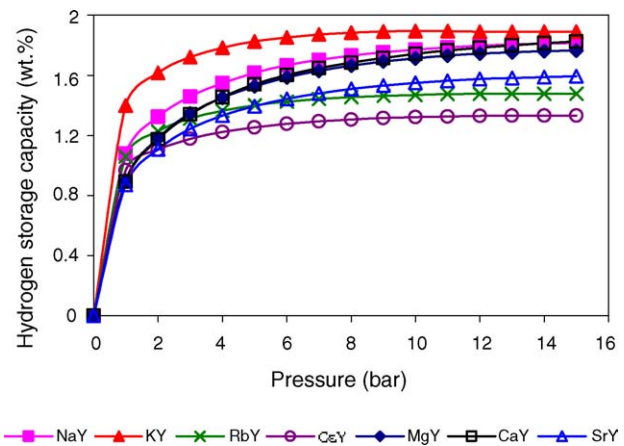
trap was used on the hydrogen gas (purity of 99.995%) inlet stream. Pressure-composition isotherms were determined at -196 °C up to 15 bar with 1 bar pressure steps. The results were corrected for buoyancy using Archimedes' principle.

3. Results and discussion

Powder X-ray diffraction patterns revealed that all the zeolites were obtained in a pure and crystalline form. The differences in lattice parameter (Table 1) reflect differences in the composition of each zeolite. The lattice parameters did not appear to follow any fixed trend, which is unsurprising as the factors affecting the lattice parameter in zeolites are complex [9]. SEM showed that each sample was made up of well-defined crystals. In none of the zeolites were there significant changes in the morphology of the crystals after ion exchange that might have indicated a degradation of the structure. Overall, high percentages of ion exchange were achieved in all materials (Table 1). BET surface area values for zeolites X and Y were significantly larger than those for the corresponding zeolites A and Rho. This suggests that, while access of nitrogen molecules to the large supercages of the FAU type zeolites was unrestricted, the penetration of nitrogen molecules into the pores of zeolites A and Rho was hindered. This behaviour may be observed because entry to the large supercages is through 12-ring windows while α -cages are accessible only through 8-ring apertures.

Table 1
Unit cell parameters, ion exchange percentages and BET surface areas of the zeolites studied

Zeolite	Unit cell parameter a (nm)	% Ion exchange	BET surface area (m^2/g)
LiX	2.476(1)	95	742 \pm 14
NaX	2.501(1)	–	662 \pm 11
KX	2.518(1)	94	607 \pm 11
RbX	2.500(1)	61	503 \pm 09
CsX	2.499(1)	66	447 \pm 08
MgX	2.503(1)	84	597 \pm 10
CaX	2.491(1)	85	669 \pm 12
SrX	2.497(2)	98	556 \pm 11
NaY	2.464(1)	–	725 \pm 13
KY	2.478(1)	98	655 \pm 12
RbY	2.465(1)	73	551 \pm 10
CsY	2.474(1)	77	470 \pm 09
MgY	2.472(1)	75	670 \pm 12
CaY	2.479(1)	79	684 \pm 12
SrY	2.477(2)	82	604 \pm 12
LiA	2.427(1)	90	1.26 \pm 0.12
NaA	2.460(1)	–	–
KA	2.467(1)	49	0.26 \pm 0.07
RbA	2.470(1)	76	0.95 \pm 0.06
CsA	2.452(1)	55	0.47 \pm 0.07
MgA	2.461(1)	78	410 \pm 07
CaA	2.449(1)	85	565 \pm 10
SrA	2.460(1)	98	391 \pm 12
NaCsRho	1.506(0)	–	3 \pm 0.19
KRho	1.488(0)	83	4.45 \pm 0.24
RbRho	1.494(0)	83	4 \pm 0.22
MgRho	1.493(0)	67	384 \pm 07
CaRho	1.449(0)	83	16 \pm 0.46

Fig. 1. Hydrogen adsorption isotherms at -196°C for zeolite X materials.Fig. 2. Hydrogen adsorption isotherms at -196°C for zeolite Y materials.

The hydrogen storage capacities of all the zeolites were determined at -196°C and 15 bar. Hydrogen uptake values reported here are accurate to ± 0.05 wt.%. The highest hydrogen storage capacity for zeolite X materials was 2.19 wt.% recorded for CaX (Fig. 1). To the best of our knowledge, this is the highest experimental hydrogen storage capacity value reported for a zeolite material (cf. 1.2 wt.% for NaX [8] and 0.7 wt.% for ZSM-5 [10]). In the case of zeolite Y materials, CaY showed the highest hydrogen uptake value of 1.82 wt.% (Fig. 2). The differences in hydrogen uptake between the various ion-exchanged FAU type zeolites cannot be accounted for on the basis of effective pore size. Both zeolites X and Y have very open frameworks and entry to most of the internal pore space is not expected to be restricted by even the largest cations. Although access is unlikely to be hindered, the ions themselves may occupy significant volumes, particularly as the larger ones may have to sit further out in the cages to have appropriate bond distances to framework oxygen atoms.

Volumetric hydrogen storage capacities derived from the observed gravimetric capacities using theoretical densities obtained from XRD data are given in Table 2. For zeolite X materials, KX and CaX had the highest volumetric storage densities of $30.2\text{ kg H}_2/\text{m}^3$ (144 H_2 molecules/unit cell)

and $31.0\text{ kg H}_2/\text{m}^3$ (143 H_2 molecules/unit cell), respectively. Meanwhile, for zeolite Y materials, KY had the highest volumetric density of $29.3\text{ kg H}_2/\text{m}^3$ (126 molecules/unit cell). It is also significant that, for the same exchangeable cation type (except Mg^{2+}), the number of hydrogen molecules adsorbed per unit cell was in all cases less for zeolite Y than for zeolite X. As zeolite Y has fewer exchangeable cations (and consequently more void space) than zeolite X, these results indicate that the interaction of hydrogen molecules with the exchangeable cations is important to the adsorption process. However, the difference was generally comparatively small considering that the number of exchangeable cations in zeolite X is approximately 60% more than that in the corresponding zeolite Y. Previous studies on the interaction of hydrogen with zeolites have reported that adsorbed hydrogen molecules interact with both the metal cations and neighbouring basic oxygen atoms of the framework [11].

At -196°C and 15 bar, NaA adsorbed 1.54 wt.% hydrogen, whereas none of the other zeolite A materials containing alkali metal cations adsorbed any appreciable amount of hydrogen (Fig. 3). The hydrogen storage capacity of CaA, in contrast, reached 1.89 wt.%. When Na^+ ions are replaced by larger K^+ , Rb^+ and Cs^+ , the effective pore size decreases

Table 2
Measured gravimetric and calculated volumetric hydrogen storage capacities at -196°C and 15 bar

Zeolite	H_2 uptake (± 0.05 wt.%)	H_2 uptake (molecules/unit cell)	H_2 uptake ($\text{kg H}_2/\text{m}^3$)
NaX	1.79	120 ± 3	25.6 ± 0.3
KX	1.96	144 ± 3	30.2 ± 0.7
RbX	1.46	122 ± 4	26.1 ± 1.0
CsX	1.32	129 ± 6	27.7 ± 1.3
MgX	1.62	102 ± 2	21.9 ± 0.7
CaX	2.19	143 ± 4	31.0 ± 0.8
SrX	1.68	127 ± 4	27.1 ± 0.6
NaY	1.81	114 ± 4	27.9 ± 1.6
KY	1.87	126 ± 4	29.3 ± 0.7
RbY	1.48	113 ± 3	27.0 ± 1.0
CsY	1.33	116 ± 3	26.3 ± 1.0
MgY	1.76	107 ± 3	25.8 ± 1.3
CaY	1.82	114 ± 3	26.6 ± 0.9
SrY	1.59	109 ± 2	25.6 ± 1.0

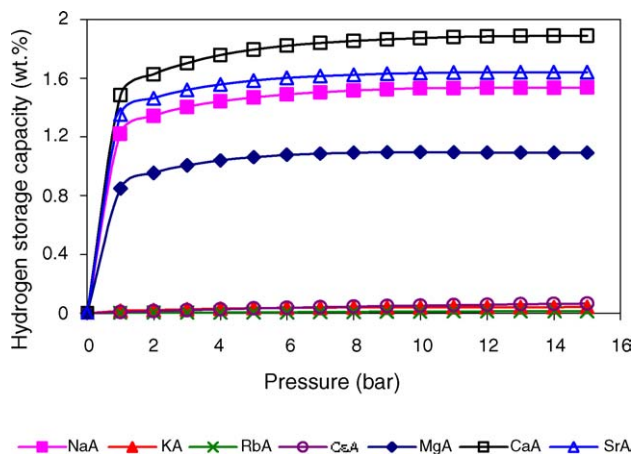


Fig. 3. Hydrogen adsorption isotherms at -196°C for zeolite A materials.

as the large cations effectively block the 8-ring that control entry into the LTA structure, thus accounting for the near zero hydrogen uptake values. It has previously been shown that the hydrogen storage capacity decreases with increasing Cs^+ content in zeolite A [12]. All the divalent cations can be accommodated in the 6-ring as there are no more than six of them (and eight 6-rings) per α -cage, leaving the 8-ring accessible to hydrogen. Pore blocking by exchangeable cations largely accounts for the significant difference in hydrogen uptake between zeolite A materials containing alkali metal cations and those containing alkaline earth metal cations. The available void volume may be another significant factor. The available void volume is related to the number and size of exchangeable cations [6]. In general, zeolites containing alkali metal cations have a large number of exchangeable cations, which occupy a substantial volume, with a consequent reduction in the space available for hydrogen uptake. MgA zeolite with an ion exchange level of 78% contained more cations than CaA and SrA, which had ion-exchange levels of 85 and 98%, respectively, and this may explain the lower uptake. The results also illustrate that although a greater number of ions occupy more space, the size of the ‘in-coming’ exchangeable cation may also be important because, apart from blocking the pores, larger cations may limit the available void volume by occupying more space themselves.

Among the different zeolite Rho materials only MgRho showed a substantial hydrogen uptake, reaching up to 1.75 wt.% (Fig. 4). Although an attempt was made to remove Cs^+ ions from zeolite Rho by carrying out NH_4^+ exchange prior to subsequent exchanges, residual Cs^+ ions in zeolite Rho could still be detected by EDX. The presence of the Cs^+ ions could at least partly explain the almost zero hydrogen uptake in the majority of zeolite Rho materials and the parent NaCsRho had practically no hydrogen uptake. This may indicate that, although the three Cs^+ ions can occupy only three of the six double-8-ring sites per unit cell, that is sufficient for total blocking to occur. The local positioning of cations has been reported to be a key factor influencing the trapping of hydrogen gas molecules in zeolite Rho [13]. The access of

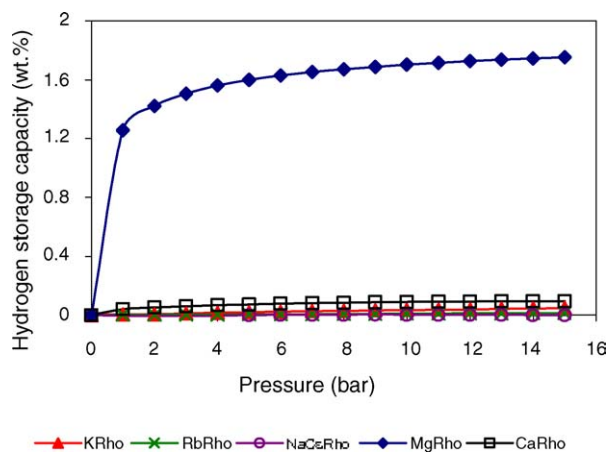


Fig. 4. Hydrogen adsorption isotherms at -196°C for zeolite Rho materials.

hydrogen to the RHO structure was least hindered in the zeolite containing not only the smallest cations Mg^{2+} , but also relatively few residual Cs^+ ions (Fig. 4). In contrast, hydrogen uptake in CaRho was approximately zero. This zeolite had two residual Cs^+ per unit cell, which is enough to block many of the double-8-rings, but it may be that the Ca^{2+} ion is itself large enough to occupy 8-ring sites. Indirect evidence for this comes from the lattice parameter of CaRho, which was substantially lower than that of other zeolite Rho materials (Table 1). This low value suggests that, unlike the other Rho zeolites, CaRho was found in the elliptical geometry [14] even in the hydrated state, which may be an indication of the presence of relatively small cations in the 8-ring sites.

In general, the hydrogen adsorption isotherms were approximately of Type I in nature according to the Brunauer classification [15], suggesting that physisorption takes place in these microporous materials. To establish whether the hydrogen uptake mechanism is a surface adsorption process the total amount of hydrogen adsorbed by each zeolite was plotted against its BET surface area (Fig. 5); a direct correlation between these two experimental parameters was found. For zeolites X and Y, hydrogen uptake relates very closely to the BET surface area. In the case of zeolites A and Rho, the scattering of the data points indicate that, the access of nitrogen molecules to the internal pore space was more restricted than that of hydrogen molecules. Hydrogen uptake has previously been shown to relate to the micropore volume in zeolites [10]. In the current work, micropore volume and pore size distribution measurements could not be derived from the nitrogen adsorption isotherms because of the limitations of the equipment used. In future, work would be carried out to relate hydrogen uptake to these parameters.

In order to explore further the surface adsorption hypothesis, experimental hydrogen uptake data were fitted to the Langmuir model [15]. In its linear form the Langmuir equation is written as:

$$\frac{p}{n} = \frac{1}{n_m b} + \frac{p}{n_m} \quad (1)$$

Table 3
Langmuir parameters for selected zeolites

Zeolite	Observed H ₂ uptake (± 0.05 wt.%)	n_m (± 0.01 wt.%)	b (bar^{-1})
NaX	1.79	1.84	3.64 ± 0.38
CaX	2.19	2.34	0.86 ± 0.04
RbY	1.48	1.53	2.19 ± 0.09
SrY	1.59	1.72	0.92 ± 0.08
NaA	1.54	1.57	3.03 ± 0.15
CaA	1.89	1.94	2.63 ± 0.01
MgRho	1.75	1.81	1.63 ± 0.09

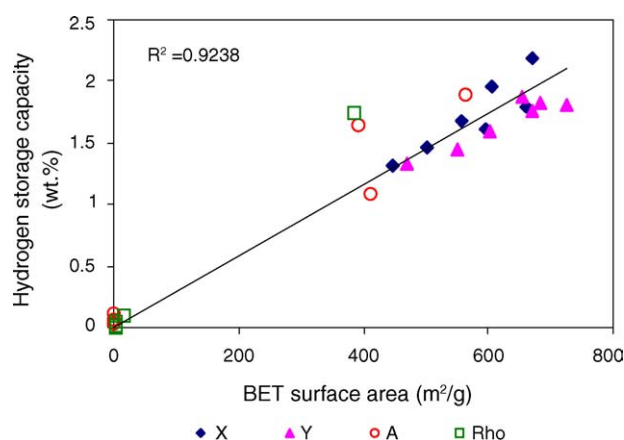


Fig. 5. Correlation between hydrogen storage capacity and BET surface area. The correlation coefficient is also indicated.

where n is the specific amount of gas adsorbed at the equilibrium pressure p of the gas; n_m the monolayer capacity and b is the adsorption coefficient, which is related to the energy of adsorption. The Langmuir plots are presented in Fig. 6 and for all materials, the plots are nearly linear over the whole pressure range of 0 to 15 bar. This suggests that the Langmuir model may be a valid representation of hydrogen adsorption on these materials. In general, the observed R -squared values (~ 1) are consistent with the applicability of the hydrogen adsorption isotherms and monolayer coverage of the zeolite internal surface. Again this indicates that the predominant mechanism underlying the present observation is physical adsorption. The derived Langmuir parameters are presented in Table 3. The observed hydrogen adsorption capacities are in good agreement with the calculated monolayer capacities. Variations in the adsorption coefficient reflect differences in the adsorption energy of the various zeolites. This suggests that the binding energies for the different cations in different frameworks vary. The Langmuir surface area derived from hydrogen adsorption was generally larger than the corresponding BET surface area derived from nitrogen adsorption and in particular, for zeolites X and Y there was a good agreement in the surface area values derived from the two methods.¹ Although the samples examined in this work generally seem to exhibit Langmuir-type behaviour, it is worth noting that long ranges of linearity in Langmuir

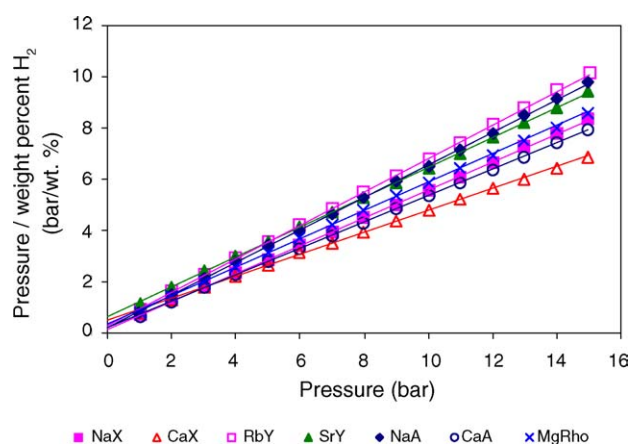


Fig. 6. Langmuir plots for the adsorption of hydrogen on selected zeolites. The correlation coefficient, $R^2 \sim 1$ in all cases.

plots do not always prove the applicability of the Langmuir model [16]. Therefore, further analysis, for example using virial equations, may provide a useful addition to the results [16].

4. Conclusions

It has been shown that for zeolites A and Rho, pore blocking by large exchangeable cations is an important phenomenon preventing hydrogen uptake. In more open zeolite frameworks (X and Y), blocking of pores by exchangeable cations is not expected. However, in addition to the large size of alkali metal cations, their presence in large numbers can affect the available void volume, thus limiting the pore space for hydrogen adsorption. A comparison between similar ion-exchanged forms of zeolites X and Y reveals that the number of hydrogen molecules stored was generally greater for zeolite X than zeolite Y suggesting that, cations act as binding sites for hydrogen molecules. Analysis of hydrogen adsorption isotherms according to the Langmuir equation indicates that physisorption is the mechanism involved. In view of the results obtained, zeolites may offer potential as low-cost, safe hydrogen storage media for stationary applications. Zeolites are advantageous because (1) they require low temperatures of synthesis and activation, (2) no CO₂ is emitted during synthesis/activation and (3) they are not flammable either in air or in a hydrogen (desorption) atmosphere. Further

¹ Results to be published elsewhere.

work involving detailed characterization needs to be carried out to explore fully the hydrogen storage and engineering properties of these materials. This includes assessing under which pressure and temperature conditions these materials may augment the storage capacity of a compressed hydrogen system.

Acknowledgements

Thanks are due to Overseas Research Student Award Scheme/Department of Metallurgy and Materials for providing funding to HWL. We also acknowledge the EU “Fuel Cell and Hydrogen Store for Integration into Automobiles” (FUCHSIA) project (part of the Framework 5 Energie Programme), and the UK Carbon Trust LCIP R&D project “The Safe, Efficient and Economic Large Scale Storage of Hydrogen”.

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