JOURNAL OF MATERIALS SCIENCE 17 (1982) 1889–1894

X-ray studies of iodine sorption in some silver zeolites

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After saturation sorption, in a static system, of molecular iodine onto some silver zeolites at 130° C, powder X-ray diffraction analysis revealed sharp reflections due to crystalline α-AgI. However, this α-AgI contained only a fraction of the sorbed iodine and it seems likely that this α-AgI involves "unlocalized" ions such that a continuous three-dimensional network of α-AgI forms in the zeolite channels. Water in the zeolite channels is probably the underlying cause: heating to 200 to 300° C in air destroyed the sharp α-AgI reflections and no such reflections were observed if the sorption was carried out with the zeolites dehydrated beforehand. α-AgI formation was enhanced when the zeolite framework was broken down by heating in air at $\gtrsim$ 800° C, heating in water or brine at 200° C, or γ-irradiation.

1. Introduction

Silver zeolites have been developed for removing radioactive iodine-bearing species from off-gases in the nuclear fuel cycle and detailed studies of the iodine sorption characteristics of such zeolites have been made with respect to efficiency, temperature, presence of water vapour and nitrogen oxides, etc. [1–5]. However, information on the atomic-scale disposition of the sorbed iodine is minimal, though X-ray studies have shown the presence of α-AgI when silver zeolite sorbs methyl iodide [5, 6]. No such information appears to exist for molecular iodine, though similar results would not be unexpected.

The present work deals with the retention and disposition of iodine in iodine-saturated zeolites after heating, γ-irradiation and mild hydrothermal treatment in water or brine, and has been carried out as part of a study of various materials or agents for the immobilization of ^{129}I, a fairly abundant waste-product of the fission process, in a nuclear waste repository. This paper, however, is primarily concerned with X-ray diffraction phenomena.

2. Experimental procedure

Commercially-prepared Ag-zeolites were examined (Table I). Appropriate quantities of zeolites and iodine crystals were sealed inside a glass container and the whole assembly was heated to about 130° C, just above the melting point of iodine, for several hours. The partial pressure of iodine vapour in the absence of sorption would have been about 0.1 MPa and about 0.05 MPa after saturation sorption had occurred. The iodine sorption (Table I) was in fair agreement with the specifications of the supplier, as expected under these conditions, because it is not very sensitive to relative humidity [2–5]. The Ag-600 sample developed a dark brown colour which could not be removed completely by subsequent heating, but which could be removed by soaking in cold water or CS_2. Analysis showed that this brown material made virtually no contribution to the iodine loading, and it appeared from its solubility in CS_2 to be chemisorbed elemental iodine.

Powder X-ray diffraction measurements were performed with a standard diffractometer, using CuKα radiation and a graphite monochromator in the diffracted beam.

Hydrothermal reaction effects were produced by sealing about 30 mg of sample and about 2 g of de-ionized water or 2 M NaCl solution in a Teflon tube and then placing the tube in an autoclave and heating to 200° C at a pressure of 5×10^7 Pa for 7 days.

γ-irradiations of about 50 M rad were per-

0022–2461/82/071889–06$03.22/0

TABLE I Commercial* zeolites studied

Trade name	Formula and type†	Physical form	Ag content (wt %)	I_2 pick-up at 130° C (wt %)	Pore size (nm)
Ag-400	$Ag_{84}Na_2Al_{86}Si_{106}O_{384} \cdot xH_2O$ Type X	1/16" diameter rods	37	20 ± 1	0.74
Ag-600	$Ag_{55}NaAl_{56}Si_{136}O_{384} \cdot xH_2O$ Type Y	20 × 40 mesh granules	28	21 ± 1	0.74
Ag-900	$Ag_{7.6}Na_{0.4}Al_8Si_{40}O_{96} \cdot xH_2O$ Mordenite	1/16" diameter rods	20	16 ± 1	0.67–0.70

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†For details, see [7, 8].

formed by placing iodine-loaded zeolites, sealed inside fused silica tubes, in a shut-down TRIGA Mark III reactor for several days. Although a higher γ-flux would have been available with the reactor running at power, neutron absorption by the Ag would have created undesirable intense long-lived radioactivity of the samples.

3. Results

3.1. Effect of heat on iodine-loaded Ag zeolite

The effect of heat on total iodine retention is shown in Fig. 1. These results agree quite well (within the order of 10%) with deductions made from gravimetric measurements on the iodine-loaded and unloaded materials and assuming no synergistic effects between the iodine and moisture contents. These gravimetric measurements were made after heating for 1 h at progressively higher temperatures at 100° C intervals and, unlike the results for the chemical analysis, weights were recorded immediately after heating to prevent significant moisture in-take from the air. Smooth curves of iodine content against temperature were obtained.

In contrast, when the iodine loading on a 13X-Ag zeolite was performed by the column technique, the iodine was virtually all retained on heating to 900° C [3]. This suggests that either the high-temperature performance of the 13X-Ag zeolite was far superior to that of each of the materials studied in the present work or that additional sorption mechanisms are operative in a static atmosphere as against a flowing system.

X-ray diffraction of the iodine-loaded products showed sharp peaks, characteristic of crystalline α-AgI, in addition to the reflections from the aluminosilicate framework. These framework reflections were reduced in intensity after iodine loading because of the increased X-ray absorption of the materials due to the presence of iodine (the patterns were observed from "infinitely-thick" samples). Although, in experiments on column-loaded materials a "loss of crystallinity" was reported to result from iodine loading [5], it seems entirely possible that the supposed loss was simply due to a reduction of the intensities of the sharp reflections through the increased X-ray absorption. The subsequent effects of heating are set out in Table II and some X-ray patterns for the Ag-400 zeolite are shown in Figs 2 and 3. Although the details are quite complex, the results can be summed up as follows. After heating at 200 to 300° C, the X-ray evidence of α-AgI vanished, but no other significant changes

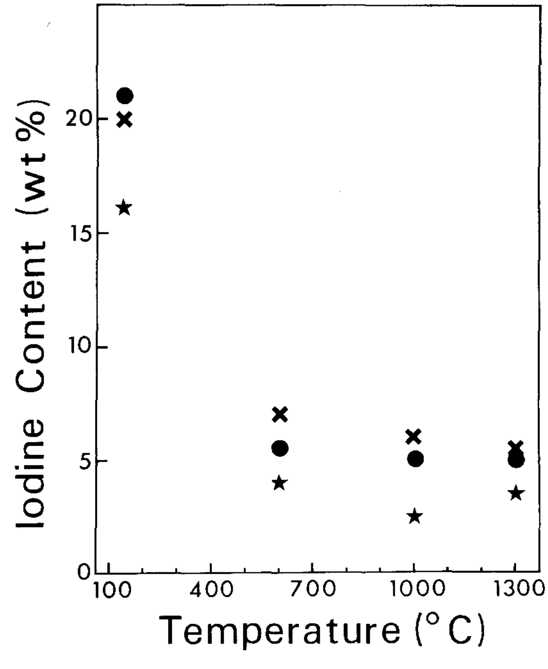

Figure 1 Iodine contents of silver zeolites loaded for several hours at 130° C in ~ 0.5 MPa partial pressure of iodine vapour. ×, Ag-400; ●, Ag-600, ☆, Ag-900. See Table I for explanation of zeolite designations. Errors in iodine analyses were approximately ± 0.5 wt%.

TABLE II Action of heat on X-ray powder diffraction patterns of silver zeolites

Heat treatment	Ag-400	Ag-600	Ag-900
Iodine-loaded			
Unheated	Crystalline zeolite + α-AgI	Crystalline zeolite + α-AgI	Crystalline zeolite + α-AgI
200° C	Crystalline zeolite + α-AgI	Crystalline zeolite + α-AgI	Crystalline zeolite
300–700° C	Crystalline zeolite	Crystalline zeolite	Crystalline zeolite
800° C	Some loss of crystallinity	Crystalline zeolite	Crystalline zeolite
900° C	α-AgI + amorphous	Trace α-AgI + amorphous	Some loss of crystallinity
1000° C	α-AgI + new aluminosilicate reflections + amorphous	α-AgI + amorphous	α-AgI + new aluminosilicate reflections + trace crystobalite + amorphous
1100° C	α-AgI + new aluminosilicate reflections + amorphous	α-AgI + amorphous	α-AgI, crystobalite + amorphous
1300° C	α-AgI + weak new aluminosilicate reflections + amorphous	α-AgI + new aluminosilicate reflections	α-AgI, crystobalite + amorphous
Not iodine-loaded			
Unheated	Crystalline zeolite	Crystalline zeolite	Crystalline zeolite
200–600° C	Crystalline zeolite	Crystalline zeolite	Crystalline zeolite
700° C	Crystalline zeolite	Crystalline zeolite	Some loss of crystallinity
800° C	Amorphous	Some loss of crystallinity	Virtually amorphous
900° C	Amorphous	Amorphous	Amorphous, quartz, metallic silver
1000° C	Amorphous	Amorphous	Crystobalite + amorphous
1100° C	Amorphous	Amorphous	Crystobalite + amorphous

occurred in the patterns. On heating at increasingly higher temperatures, no further changes in the patterns ensued until after heating at ≈ 800° C when the framework began to lose its crystallinity. Sharp reflections due to α-AgI appeared concurrently. For the Ag-600 and Ag-900 zeolites, but not the Ag-400 material, these reflections had considerably more intensity than those in the unheated iodine material, even though the iodine content after heating at ≈ 800° C was considerably less than that before heating (Fig. 1). This result showed that in the unheated Ag-600 and Ag-900 material, only a fraction of the sorbed iodine was in the α-AgI form. However, for all the zeolites, hydrothermal treatment (see below) increased the intensities of the α-AgI reflections so the α-AgI in

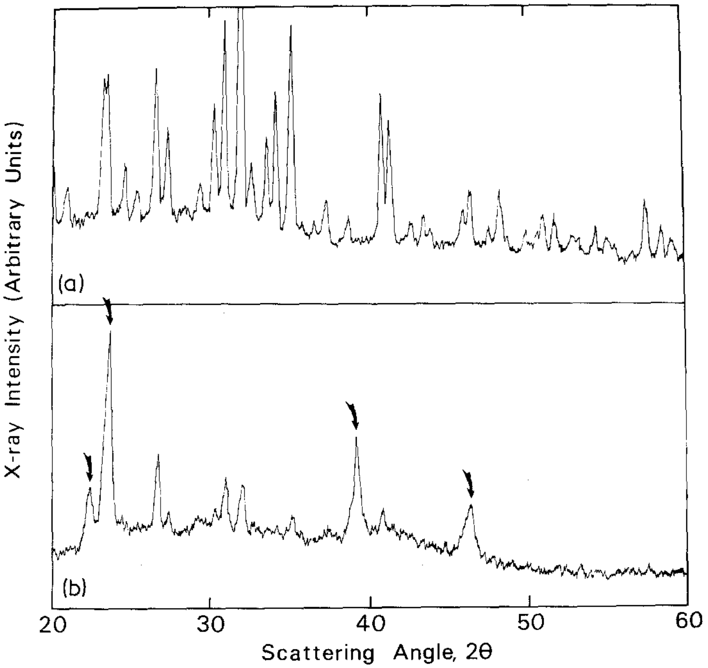

Figure 2 Effect of iodine loading on X-ray pattern of silver zeolite, Ag-400. Top = (a) Unloaded zeolite, (b) iodine-loaded zeolite. Arrowed peaks are characteristic of α-AgI. The α-AgI peaks were relatively weaker for the Ag-600 and Ag-900 zeolites. CuKα radiation.

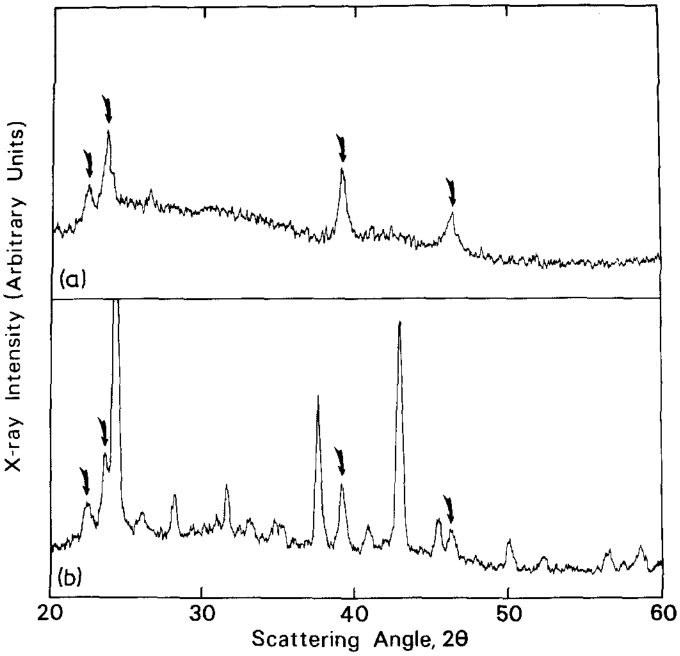

Figure 3 Effect of heating on X-ray pattern of iodine-loaded silver zeolite Ag-400. Arrowed peaks are characteristic of α-AgI. (a) Heated at 900° C; (b) heated at 1100° C; the strongest of the unarrowed peaks are apparently due to a sodalite-analogue phase [$(Na, Ag)_4Al_3Si_3O_{12}I$] [9] but a few of the weaker peaks derive from mullite. CuKα radiation. Somewhat surprisingly, the lattice parameter of the sodalite-analogue phase was found to be 0.893 ± 0.001 nm. This value is slightly smaller than that of pure $Na_4Al_3Si_3O_{12}I$ [10], even though Ag^+ is a larger ion than Na^+ [11].

the Ag-400 zeolite did not contain all the sorbed iodine either. After heating at still higher temperatures, sharp reflections due to α-AgI remained and some recrystallization of the aluminosilicate took place. Table II shows the changes which occurred on heating for both unloaded and iodine-loaded material. The iodine loading had a mild effect on the response of the framework to heat.

3.2. Hydrothermal and γ-irradiation effects

X-ray patterns of the residual solid material after the hydrothermal treatment revealed an enhancement of the α-AgI reflections and partial loss of crystallinity and/or alteration of the aluminosilicate framework. No systematic differences were observed whether water or the 2 M NaCl solution was used (extra reflections due to NaCl were observed in the air-dried solids recovered from the 2 M NaCl runs). Because of the presence of soluble iodine in the Ag-600 sample at least, (see above) no solution analyses were performed. However, comparative experiments in deionized water at 200° C on precipitated α-AgI revealed no detectable Ag^+ or I^- in solution, or any recrystallization of the AgI, so it was assumed that all the sorbed iodine in the form of molecular or crystalline silver iodine would be similarly resistant to hydrothermal treatment.

Although a ^{129}I-loaded Ag zeolite would experience only a very small radiation dose from the decay of ^{129}I itself, conditions in a nuclear waste repository would doubtless be such that a zeolite would receive an appreciable γ-dose from other waste. After the approximately 50 M rad γ-dose two of the three zeolites showed observable structural effects.

The X-ray results for hydrothermal treatment and γ-irradiation are set out in Table III.

4. Discussion

It was mentioned previously that the iodine, apparently in crystalline α-AgI in the iodine-loaded zeolites before heating, comprised only a small fraction of the sorbed iodine and that this

TABLE III X-ray effects of hydrothermal treatment and of γ-irradiation on iodine-loaded Ag-zeolites

Ag-zeolite	Effects of Hydrothermal (200° C) treatment	Effect of ~ 50 MRad of γ-irradiation
Ag-400	Some loss of crystallinity and alteration of framework; α-AgI reflections enhanced	α-AgI reflections enhanced somewhat
Ag-600	Considerable loss of crystallinity and alteration of framework; α-AgI reflections markedly enhanced	α-AgI reflections considerably enhanced
Ag-900	Some modification to framework; α-AgI reflections considerably enhanced	Virtually no change

α-AgI could be removed by relatively gentle heating (at about 300° C).

To explain the sharpness of the X-ray Bragg diffraction reflections from the α-AgI in the unheated material, crystallites having sizes $\gtrsim 50$ nm in each dimension are required. If α-AgI did form as $\gtrsim 50$ nm-sized crystallites in voids, imperfections, etc., it would not be easy to explain the disappearance of the crystallites on heating at about 300° C. [Although 300° C exceeds the α–β transformation temperature (146° C) it is well below the melting point (558° C).]

It seems more likely that the α-AgI forms a continuous network in the open channels in these zeolite materials. Since the α-AgI is observed in different zeolites characterized by different lattice and interatomic spacings, the Ag^+ ions involved cannot be fixed directly to the zeolite lattices. The as-received zeolites had been heated in hydrogen at 500° C, so it would be highly likely that much of the Ag would be in the atomic form. Absorption of elemental iodine to form molecular AgI could then take place without charge changes on other ions in the zeolites.

The unlocalized Ag^+ ions in the zeolites studied in the present work could simply derive from the presence of water in the zeolitic channels; the removal of the water would tend to force the Ag^+ ions back to more definite positions within the zeolite framework [7, 8]. This would break up the continuous α-AgI network and would explain why α-AgI was removed on heating of the zeolites at 200 to 300° C; water would have been removed by such treatment. The AgI would now be in molecular form and, as such, would not give sharp X-ray reflections. Evidently the re-absorption of H_2O on exposure to the air in the laboratory after cooling was unable to shift the relevant Ag^+ ions appreciably and allow the continuous network of α-AgI to re-form.

To further examine this point, the sorption experiments were repeated using the dehydrated zeolites. The unloaded zeolites and iodine were placed in a glass tube and continuous evacuation with a rotary pump was performed, the iodine being "down-stream" in the line. The zeolites, but not the iodine, were heated to about 400° C to dehydrate them while evacuation continued. After cooling, the tube was sealed off and iodine was sorbed onto the zeolites by heating the whole assembly to 130° C. (Gravimetric work and X-ray fluorescence analysis in a control experiment showed that a minor amount of iodine was sorbed before this latter heating.) The iodine loadings were similar to those found previously. No α-AgI reflections were observed in subsequent X-ray patterns as expected by the above; there would have been no unlocalized Ag^+ ions or Ag atoms in the dehydrated zeolites. The changes of the X-ray patterns of these loaded materials on heating above about 800° C were similar to those indicated in Table II.

The observation that the iodine loadings in the zeolites which were dehydrated before loading were similar to the loadings in the corresponding zeolites which were not dehydrated before loading, suggests that the presence of H_2O is not critical for the sorption of elemental iodine. To further explore this point, observations were made of the species evolved from the iodine-loaded zeolites which were not dehydrated before loading. The samples were heated at a rate of about $5°\,C\,min^{-1}$ up to about 400° C in a glass system and maintained at this temperature for several hours. The evolved materials which condensed at room temperature were principally molecular iodine and water. Essentially, no water-soluble species which remained as gases at room temperature (such as HI) were observed. Subsequent X-ray diffraction analysis confirmed the removal of the evidence of α-AgI.

The break-down of the zeolite structure by the action of dry heat at about 800° C, aqueous media at 200° C, and γ-irradiation (via radiolysis effects on included water, see, for example [12]) presumably allows the AgI molecules to migrate and aggregate to form three-dimensional crystallites. The retention of some α-AgI after heating to temperatures as high as 1300° C is probably not surprising as the boiling point of AgI is 1506° C [13], even though its melting point is only 558° C [13].

Other features of interest in the system were (a) the high degree of iodine loss on heating to $\lesssim 600°$ C (compared with [3]), (b) the origin of the plates, supposedly of α-AgI, observed by scanning electron microscopy in CH_3I-loaded zeolite [5], and (c) the relative constancy of the iodine contents of each sample on heating from 600 to 1300° C.

Firstly, the loss of iodine over the 130 to 600° C range would not seem to be due to iodine in the AgI form (since AgI would not be volatile), so, as deduced from the measurements made in the glass system, the iodine responsible was probably in chemisorbed elemental form.

Secondly, optical microscopic examination revealed small black iodine crystals in the interior of the Ag-900 zeolite examined in the present work. These could easily be confused with α-AgI crystals in scanning electron microscopy.

Thirdly, the relative constancy of the iodine contents of heating over the 600 to 1300° C range probably means that in the 600 to 800° C range, before the break-down of the zeolite framework, the iodine exists as molecular AgI. The destruction of the framework on heating beyond 800° C appears to allow the molecular AgI to aggregate and to form a network of α-AgI (noting that this would be molten at the heating temperature).

Finally, we have made a cursory examination of a Pb-zeolite (Pb-400, an analogue of Ag-400). This material would not absorb appreciable elemental iodine by the technique used for the silver zeolite but would take up about 20 wt% I in a HI atmosphere (see also [2]). X-ray diffraction of the loaded material showed strong PbI_2 reflections.

5. Conclusions

The sorption of elemental iodine on silver-zeolites is apparently a rather complex process but some progress has been made in its elucidation. More definitive studies will require the use of single-crystal X-ray diffraction, possibly supplemented by Raman and infra-red spectroscopy, on materials loaded in both static and flowing atmospheres.

Acknowledgements

We thank Dr K. K. S. Pillay for performing the reactor irradiations, Mr S. D. Atkinson for performing solution analyses, and an anonymous reviewer for helpful comments on an earlier draft of this manuscript. This research was performed under subcontract with Rockwell International under Contract number DE–AC09–79ET41900 with the Department of Energy.

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Received 28 October
and accepted 16 November 1981