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ScienceDirect
Applied Radiation and Isotopes 65 (2007) 259–265
Applied Radiation and Isotopes
www.elsevier.com/locate/apradiso

Immobilization of cobalt in collapsed non-irradiated and γ-irradiated X zeolites

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Received 10 November 2004; received in revised form 18 July 2006; accepted 31 July 2006

Abstract

Cobalt exchanged X zeolites were gamma irradiated and heated until the zeolite structure collapsed. Heating destroys the zeolite network as found by X-ray-diffraction and ^{29}Si, ^{27}Al MAS NMR spectroscopy. Gamma irradiation treatment diminished the collapsing temperature of zeolite. Cobalt leaching from crystalline and amorphized zeolites was verified by ion exchange with NaCl solution. Results show that cobalt is not released from the amorphous materials. Furthermore adsorption of xenon and ^{129}Xe NMR spectroscopy reveal that cobalt ions are heterogeneously distributed in the non irradiated amorphous materials. Gamma irradiation causes the mobility of cobalt in the amorphous materials resulting then in a more homogeneous distribution. Cobalt is, thus, retained safely in the amorphous materials.

Keywords: Cobalt; Zeolite; Vitrification; Xenon; Irradiation; Radioactive waste; Adsorption; Glass; Vitreous

1. Introduction

The safe treatment and disposal of radioactive wastes are difficult (Thamzil, 1997). Retention of radionuclide in zeolites is a procedure proposed to purify waters containing radionuclides (Kallo, 2001). Indeed, zeolites were the exchangers used to trap some radioactive cations in the Chernobyl and the Three Mile Island accidents (Siemens et al., 1982; Chelishchev, 1993). However, the radionuclides trapped in zeolites may leach (Dyer and Abou-Jamous, 1997; Dyer and Aggarwal, 1997), thus their use to store radioactive materials for long time periods remains controversial . Waste waters may contain ^{60}Co, which is a radionuclide (γ-emitter) with a long half-life, emerging mainly from the nuclear industry and hospitals. For a safe and long-time retention of the radioactive cobalt, the exchanged zeolites have to be vitrified. This step is not obvious. It has been shown (Bulbulian and Bosch, 2001) that at 900 °C, CoA and CoX zeolite networks collapse but a recrystallization of carnegeite, nepheline and cobalt aluminate is observed. Although a fraction of the ions is retained in the crystalline structures, another fraction remains in the amorphous or glassy materials that are characterized by an irregular structure, but even these groups of materials possess some structural layers (Fripiat et al., 1971; Leadbetter and Wrigth, 1972) because of structural phase transitions. The collapsing of cobalt exchanged zeolites may result in a safe cobalt retention. This is possible if the cations are occluded in the amorphous material. However, if a glassy structure is submitted to high doses of irradiation, it may develop defects and cracks favourable to the releasing of the radionuclides. In this case, the radiation effects on the materials exchanged with radioactive species need to be deeply characterized. In a previous work (Lima et al., 2004), we characterized cobalt exchanged zeolites that were thermally treated and gamma irradiated. We showed that fractal dimension, a morphological parameter, could be

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doi:10.1016/j.apradiso.2006.07.011

correlated with cobalt leaching. However, this correlation is only valid if zeolites maintain their crystallinity. The distribution of cobalt and the fractal dimension appears to be a determining factor in the safe retention. As far as we know, this has not been discussed in the literature.

The aim of this work is to study the cobalt distribution in the crystalline zeolites and amorphous materials, both non- and γ-irradiated. The chemical environment of aluminium and silicon atoms may be determined by ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR). The porosity of the material can be characterized through xenon sorption and ^{129}Xe NMR spectroscopy as the chemical shift is very sensitive to the local electron densities (Fraissard and Ito, 1988; Springuel-Huet et al., 1995).

2. Materials and methods

2.1. Materials

Powdered X zeolite in the Na^+ form with the composition: $Na_{12}Si_{12}Al_{12}O_{48} \cdot xH_2O$, supplied by Union Carbide was used as starting material. Cation exchange with $Co(NO_3)_2$ was performed as described elsewhere (Bulbulian and Bosch, 2001). Briefly, 20 g of sodium zeolite X was added to 400 ml of 0.05 N cobalt nitrate solution at room temperature. The mixture was shaken for 3 h. Solid was separated by centrifugation and then washed with deionized water. Exchanged cobalt zeolites are denoted as CoX.

The cobalt content in the CoX solid was determined by neutron activation analyses as follows: samples were irradiated in a Triga Mark III nuclear reactor for 15 min with an approximate neutron flux of 10^{13} n/cm^2 s. The 1170 and 1330 photo peaks from ^{60}Co produced by the nuclear reaction $^{59}Co(n,\gamma)^{60}Co$ were measured with a Ge/hyper-pure solid-sate detector coupled to a computerized 4096 channel pulse height analyzer. The cobalt content of CoX zeolite was 0.86 meq/g zeolite.

The CoX samples were thermally treated in air at 700 and 900 °C. The resulting materials are labeled CoX-700 and CoX-900, respectively, and they are the matter of this work. These samples were then γ-irradiated in a ^{60}Co γ-beam at 1 and 6 MGy.

2.2. Characterization

X-ray diffractograms were obtained in a Siemens D 500 diffractometer coupled to a copper anode X-ray tube. The copper Kα wavelength was selected using a Ni filter.

^{27}Al and ^{29}Si MAS NMR spectra were recorded on a Bruker ASX-300 spectrometer operating at a resonance frequency of 78.21 and 59.63 MHz, respectively.

Samples for ^{27}Al MAS NMR measurements were packed in ZrO_2 rotors having an o.d. of 4 mm. A single $\pi/2$ pulse of 2 μs was used and a recycle time of 0.5 s was applied. Rotors were spun at 10 kHz. Chemical shifts were referenced to a 0.1N $AlCl_3$ solution.

^{29}Si MAS NMR spectra were acquired with a pulse length of 3 μs and a recycle time of 8 s. Rotors for these experiments were spun at 5 kHz. Chemical shifts were referenced to TMS.

Xenon gas (Praxair, 99.999%) was used for the ^{129}Xe NMR experiments. The sample powder was placed in a NMR tube equipped with J. Young valves, through which xenon gas was equilibrated with the sample at 18 °C under different pressures. Previous to xenon loading, samples were dehydrated by gradual heating up to 400 °C in vacuum ($<10^{-4}$ Torr). ^{129}Xe NMR spectra were recorded at 18 °C in a Bruker DMX-500 instrument operating at 138.34 MHz for ^{129}Xe. The chemical shift was referenced to xenon gas extrapolated to zero pressure. The spectra of crystalline samples were recorded with at least 1000 scan with delay time of 2 s. As the amorphized samples adsorbed a minor amount of xenon, the scan number to obtain the spectra of these samples was at least 2000.

3. Results

Fig. 1 compares the X-ray diffraction patterns of the CoX zeolites, untreated and thermally treated at 700 and 900 °C. The crystallinity of CoX zeolite is maintained up to 700 °C. However, at 900 °C the sample turned out to be amorphous and small amounts of nepheline, carnegeite and cobalt aluminate were also present. The X-ray diffraction patterns of the thermally treated and gamma-irradiated zeolites do not reveal any influence of radiation on the amount of crystalline materials.

Cobalt desorption was promoted by a secondary exchange of the cobalt containing samples with a 1 N solution of NaCl. Results established that CoX-700 and CoX-900 leach 32% of the total cobalt of the CoX zeolite. In contrast, CoX-900 leached a very small amount (less than 0.2%). Another important result was that γ-irradiation enhanced the retention of cobalt in crystalline or amorphous samples. The cobalt leaching values, taken from our previous work (Bulbulian and Bosch, 2001) are reported in Table 1.

^{27}Al MAS NMR spectra of CoX-700 samples (Fig. 2), show that in crystalline samples, the aluminium is tetrahedrally coordinated (resonance at 62 ppm) but a fraction of aluminium tetrahedra is distorted (resonance at 42 ppm) (Samoson and Lippmaa, 1983; Samoson et al., 1987). As the sample is irradiated the tetrahedral distorted signal becomes more intense than the non-distorted. As the temperature is increased up to 900 °C, only one broad peak is observed with a maximum at 44 ppm (Fig. 2).

^{29}Si MAS NMR spectra of CoX samples heated at 700 °C (Fig. 3), exhibit the typical signals: ^4Q(Si-0Al) at −107 ppm, ^4Q(Si-1Al) at −98 ppm, ^4Q(Si-2Al) at −93.2 ppm, and ^4Q(Si-3Al) at −88.5 ppm (Fyfe et al., 1984). The irradiation of CoX-700 samples modifies strongly the intensities of the peaks. Indeed, the peaks

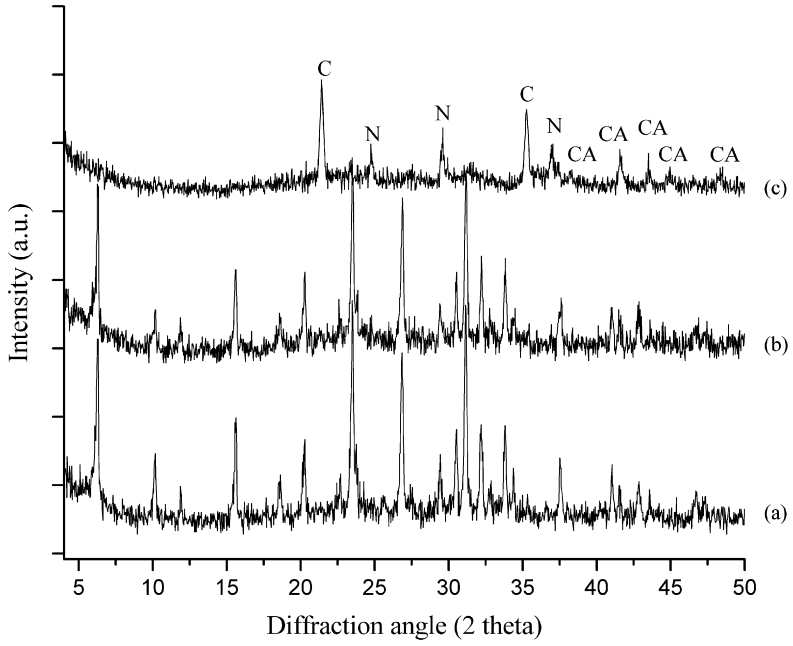

Fig. 1. X-ray diffraction patterns of the CoX, CoX-700 and CoX-900 samples, (a), (b) and (c) respectively. (C) carnegeite, (N) nepheline, (CA) cobalt aluminate.

Table 1
Cobalt desorption from CoX zeolites

Sample	γ-irradiation dose (MGy)	Cobalt leaching (%)[a]
CoX-700	0	48
	1	40
	6	31
CoX-900	0	0
	1	0
	6	0

[a]Values taken from Bulbulian and Bosch (2001).

^{4}Q(Si-2Al) and ^{4}Q(Si-3Al) diminish as those assigned to ^{4}Q(Si-0Al) and ^{4}Q(Si-1Al) increase. The effect of γ-irradiation on ^{29}Si MAS NMR spectra is confirmed if each contribution of ^{4}Q(Si-*n*Al) to ^{29}Si MAS NMR spectra is calculated (Fig. 4 and Table 2).

Xenon adsorption isotherms are shown in Fig. 5. Crystalline sample clearly adsorb more xenon than amorphous material. The amounts of xenon adsorbed in crystalline zeolites, as a function of xenon pressure, are in agreement with those reported in the literature for similar compounds (Kim et al., 1994). We did not find any previous study on xenon adsorption in amorphous aluminosilicate materials.

Fig. 6 shows the ^{129}Xe NMR spectra. The following remarks can be listed:

(1) All spectra include the very broad peak whose maximum is close to 280 ppm.

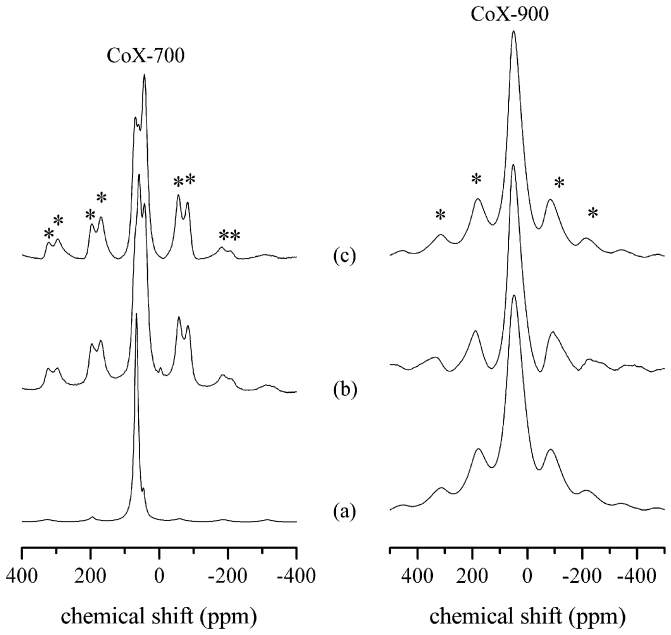

Fig. 2. ^{27}Al MAS NMR spectra of CoX-700 and CoX-900 samples non-irradiated (a), and γ-irradiated at 1 MGy (b) or 6 MGy (c). Peaks labeled * are spinning side bands.

(2) The crystalline sample (CoX-700) exhibits a high-field signal (75 ppm) that diminishes when the sample is submitted to γ-beam. No significant changes are observed for the two different irradiation doses used.
(3) The intensity of the signal at strong field (75 ppm) in spectra recorded for amorphous samples is much less intense than the signal obtained with crystalline

samples. However the intensity of this signal remains unchanged if the samples are irradiated.

4. Discussion

To summarize, our previous results showed that the samples CoX-700, non-irradiated or γ-irradiated, were crystalline. No effect of irradiation on the aluminosilicate structure was revealed. In contrast, CoX-900 sample was composed mainly of an amorphous material; the γ-irradiation, again, had no influence on the global structure of the sample as determined by X-ray diffraction. However in all cases the γ-irradiation enhanced the retention of cobalt.

^{27}Al MAS NMR results (Fig. 2), show that some tetrahedral aluminium (signal at 62 ppm) can be distorted

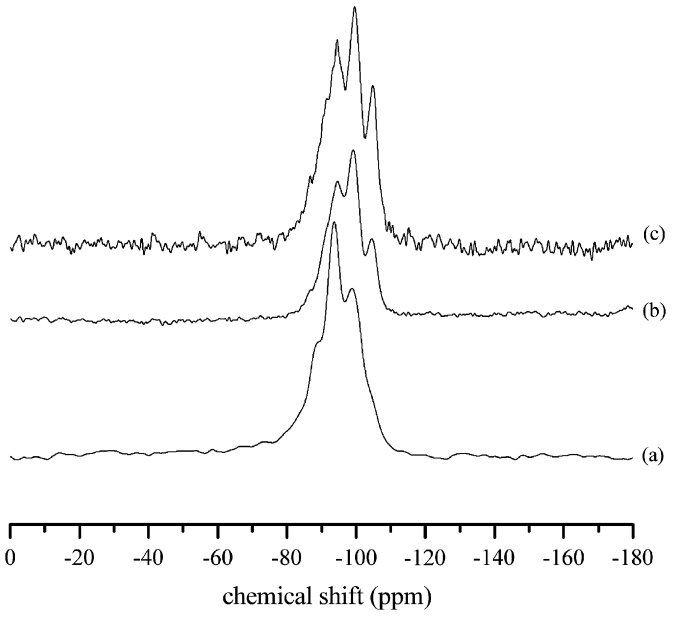

Fig. 3. ^{29}Si MAS NMR Spectra of CoX-700 samples non-irradiated (a) and γ-irradiated at 1 MGy (b) or 6 MGy (c).

Table 2
Deconvolution of ^{29}Si MAS NMR spectra

Simple	Gamma irradiation dose (MGy)	δ_{iso} (ppm)/^{4}Q(Si-nAl)	Distribution (%)	[a]Si/Al ratio
CoX-700	0	−90/^{4}Q(Si-3Al)	15	2.4
		−95/^{4}Q(Si-2Al)	45	
		−100/^{4}Q(Si-1Al)	30	
		−106/^{4}Q(Si-0Al)	10	
	1	−89/^{4}Q(Si-3Al)	6	3.9
		−94/^{4}Q(Si-2Al)	19	
		−100/^{4}Q(Si-1Al)	42	
		−107/^{4}Q(Si-0Al)	33	
	6	−90/^{4}Q(Si-3Al)	4	4.3
		−94/^{4}Q(Si-2Al)	15	
		−102/^{4}Q(Si-1Al)	57	
		−108/^{4}Q(Si-0Al)	24	
CoX-900	0	−91/^{4}Q(Si-3Al)	20	3.6
		−96/^{4}Q(Si-2Al)	13	
		−101/^{4}Q(Si-1Al)	14	
		−108/^{4}Q(Si-0Al)	53	
	1	−90/^{4}Q(Si-3Al)	19	3.8
		−96/^{4}Q(Si-2Al)	8	
		−100/^{4}Q(Si-1Al)	35	
		−108/^{4}Q(Si-0Al)	38	
	6	−93/^{4}Q(Si-3Al)	18	3.9
		−97/^{4}Q(Si-2Al)	5	
		−100/^{4}Q(Si-1Al)	48	
		−107/^{4}Q(Si-0Al)	29	

[a]Si/Al ratio calculated from integrated intensities using the procedure reported in Rumori (2000) and Samoson et al. (1987).

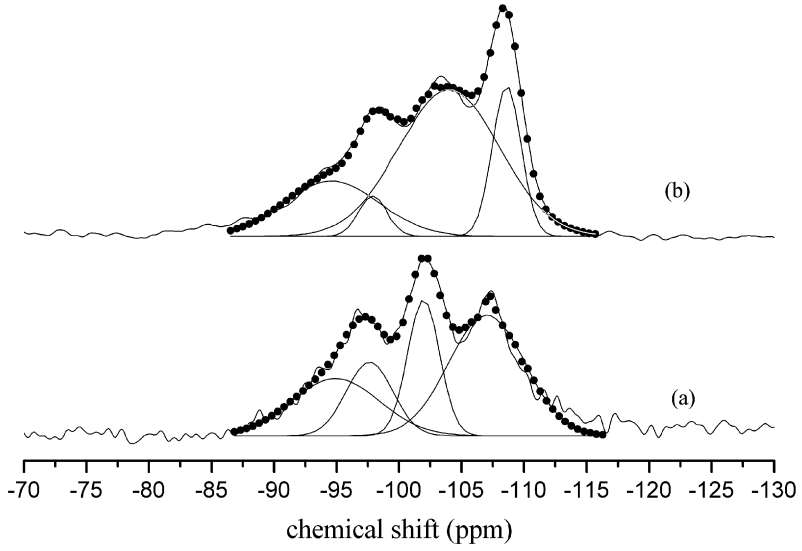

Fig. 4. ^{29}Si MAS NMR Spectra of CoX-900 samples non-irradiated (a) and γ-irradiated at 6 MGy (b). The solid lines correspond to each individual contribution and their sum. The points represent the experimental spectrum.

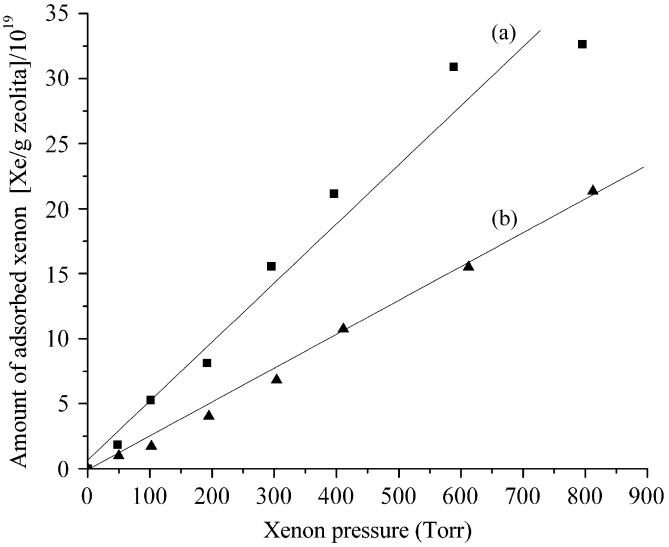

Fig. 5. Xenon adsorption isotherms on CoX-700 (a) and CoX-900 (b) samples.

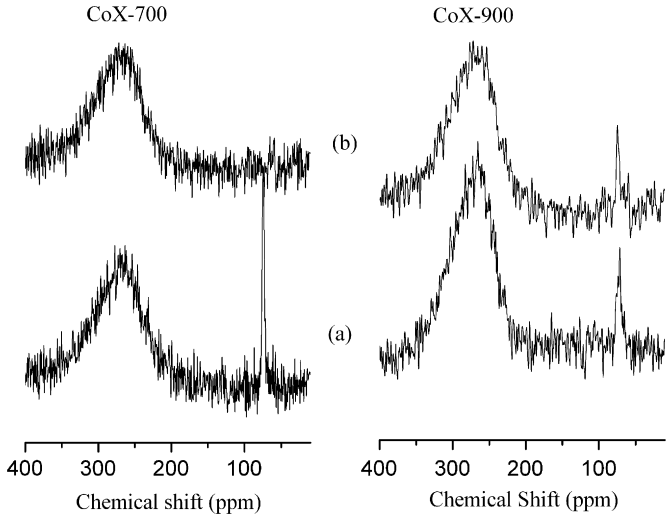

Fig. 6. ^{129}Xe NMR spectra of xenon sorbed in samples CoX-700 and CoX-900, non-irradiated (a), or γ-irradiated (b).

in CoX-700 sample. No octahedral aluminium was detected. The classical aluminium tetrahedral present in the zeolitic structure became distorted as the samples were heated and γ-irradiated. This aluminium is stable enough and does not cause zeolite collapse. The global structure of zeolite is maintained in agreement with the XRD study, but local modifications occur as supported by ^{27}Al MAS NMR results. The ^{29}Si MAS NMR spectra included in Figs. 3 and 4 confirm this hypothesis. Indeed, the dealumination induced by γ-irradiation is clearly revealed (Table 2). Thus, the signal ^{4}Q(Si-0Al) at -107 ppm clearly increases as the peaks ^{4}Q(Si-2Al) and ^{4}Q(Si-3Al) decrease, at -93.2 and -88.5 ppm, respectively.

The dealumination of zeolite as the samples are irradiated is clear from ^{29}Si MAS NMR spectra. Si/Al ratio, evaluated from ^{29}Si MAS NMR spectra (Loewenstein, 1954; Fyfe et al., 1984), increases from 2.4 to 4.3 when the CoX-700 sample is non-irradiated or γ-irradiated at 6 MGy. We concluded in our previous works (Bulbulian and Bosch, 2001; Lima et al., 2004) that the γ-irradiation enhances the retention of cobalt but this was not directly associated to non-framework aluminium. Note that if zeolite dealumination is promoted by gamma irradiation the excess aluminium should segregate as an amorphous compound not detected by XRD. In this sense, the ^{27}Al NMR results are more representative as they showed the alteration of the aluminium coordination.

Concerning the presence of the cobalt in the free spaces of the materials, the ^{129}Xe NMR results are more useful. The xenon is a selective probe molecule of supercages in faujasites since xenon atom (0.43 nm) can enter only into the supercage through the 0.74 nm pore aperture. Xenon cannot enter into sodalite cages due to the smaller pore aperture (0.22 nm). The broad peak in ^{129}Xe NMR of xenon sorbed in CoX-700 confirms the presence of Co^{2+} in the large cavity of the X zeolite as the paramagnetic nature of this cobalt oxidation state causes a shorter relaxation of the NMR signal. However, a non-expected result is observed: A second peak (74 ppm), less broad than the peak at 267 ppm is obtained. The presence of two peaks is characteristic of metal heterogeneously distributed (Menorval et al., 1985; Guillemot et al., 1997; Rumori, 2000). Most probably, in non-irradiated CoX-700, cobalt is heterogeneously distributed, there are zones cobalt enriched and some others with a higher sodium content. If this sample is gamma-irradiated, the peak at weaker fields fades out. Then, the γ-irradiation induces the motion of both cations. Then, in the resulting sample the metal is more homogeneously distributed. This homogeneous distribution of cobalt can be correlated with the lower cobalt leaching of irradiated crystalline zeolites.

In the ^{129}Xe NMR spectrum of the non-irradiated CoX-900 sample, two peaks are observed but one of them is much less intense and broad than the other. Again, as in crystalline samples, cobalt seems to be heterogeneously distributed. X-ray diffraction results show that the sample is composed of carnegeite, nepheline cobalt aluminate and amorphous material. Therefore, it has to be concluded that a part of cobalt is trapped in the aluminate cobalt as an element of the lattice. As this compound cannot adsorb Xe, the signal in ^{129}Xe NMR spectra can only be due to the xenon adsorbed on the amorphous fraction. When CoX-900 sample was irradiated, the ^{129}Xe NMR spectra were not modified. The Si/Al ratio of amorphous materials irradiated or not, remains almost unmodified showing the stability of cobalt cations against the irradiation. It seems then that cobalt is immobilized and consequently safely retained. A model representing this behaviour is included in Fig. 7: The crystalline CoX zeolite behaves differently depending on the treatment received. On the one hand, if zeolite is gamma irradiated, the zeolitic structure is partially maintained but local amorphization occurs, in this case the cobalt cations are redistributed as the zeolite is

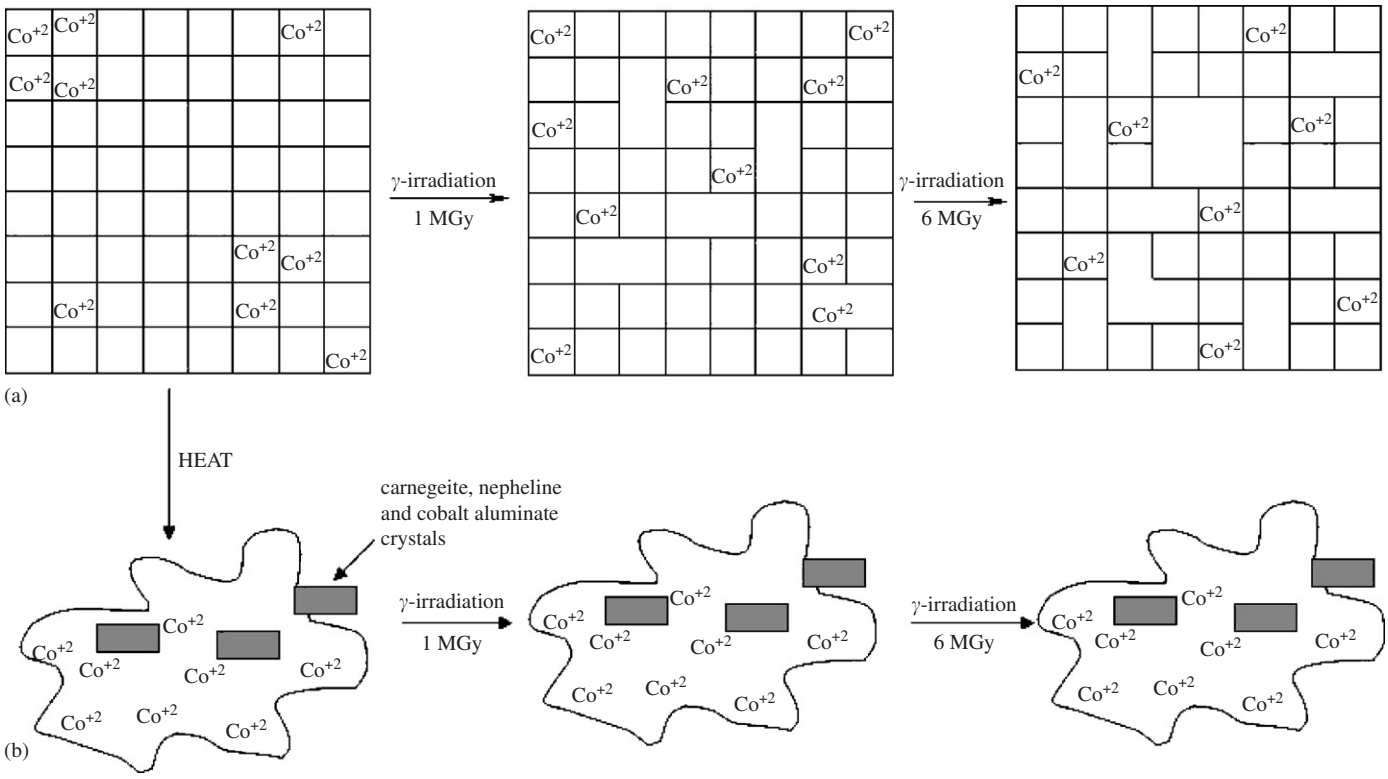

Fig. 7. Evolution of cobalt positions in non-irradiated and gamma-irradiated zeolite X. Crystalline samples (a) and amorphized samples (b).

irradiated. On the other hand, if the cobalt containing zeolite is thermally treated the framework collapsing is promoted and cobalt is retained by two ways, in the first one the cobalt cations are occluded in the amorphous material and in the second one, the cobalt is incorporated as small crystallites of cobalt aluminate a non-exchanger material.

5. Conclusion

The distribution of cobalt in exchanged X zeolites, treated at 700 or 900 °C and irradiated at 1 or 6 MGy, varies. In CoX-700 treated samples, which maintain the zeolite structure, cobalt is found in the large cavities but irradiation redistributes it. Cobalt leaching, then, is lower.

Instead, with a thermal treatment at 900 °C the exchanged zeolite looses its crystallinity and a mixture of carnegeite, nepheline, cobalt aluminate and amorphous compound is obtained. Cobalt is present as an element of the crystalline cobalt aluminate but its presence in the amorphous compound could not be excluded. In this sample cobalt does not leach, independently of the irradiation dose.

Acknowledgment

Conacyt (Mexico) Grant no. J49009 is gratefully acknowledged. The technical help of M.A. Vera (UAMI) is appreciated.

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