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

Enrique Lima[a,b,*], Pedro Bosch[a], Silvia Bulbulian[c]

[a]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 México D.F., Mexico
[b]Universidad Autónoma Metropolitana, Iztapalapa, Av. San Rafael Atlixco No. 186 Col. Vicentina, 09340 México D.F., Mexico
[c]Instituto Nacional de Investigaciones Nucleares, Col. Escandón, Delegación Miguel Hidalgo, 11801 México D.F., Mexico

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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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*Corresponding author. Departamento de Química, Universidad Autónoma Metropolitana, Iztapalapa, Av. San Rafael Atlixco No. 186 Col. Vicentina, 09340 México D.F., Mexico. Tel.: +525 55804 4667; fax: +525 55804 4666.

E-mail address: lima@xanum.uam.mx (E. Lima).

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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: ^{4}Q(Si-0Al) at −107 ppm, ^{4}Q(Si-1Al) at −98 ppm, ^{4}Q(Si-2Al) at −93.2 ppm, and ^{4}Q(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