Fractal Dimension and Cobalt Leaching in CoX and CoA Zeolites

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Cobalt-exchanged A and X zeolites are studied by infrared spectroscopy and small-angle X-ray scattering. Samples were irradiated and heated until the zeolite structure collapsed. We found that cobalt leaching depends on the fractal dimension regardless of the nature of the zeolite and the irradiation treatment. Heating and γ-irradiation destroys the zeolite network as found by infrared spectroscopy. The modifications in the 4R and 6R pore opening vibrations show that the cobalt sites are altered by thermal and irradiation treatments.

Introduction

The nuclear industry produces large amounts of radioactive wastes, the safe treatment and disposal of which is difficult. Nuclear wastewaters can be treated by circulation through columns containing zeolites and clays,[1] or by other methods. But radioactive materials trapped by cation exchange in zeolites may not be safe enough, as the radionuclides can be exchanged again through the same mechanisms in the presence of water. To avoid this process the exchanged aluminosilicates may be incorporated into cement casts,[2] occluded with large cations such as barium,[3] or thermally treated to immobilize the radioactive materials in a glassy lattice.

In a previous work[4] we found that cobalt is irreversibly trapped in thermally treated zeolites A and X at temperatures higher than 800 °C. Although the radiation coming from the encapsulated elements in the vitrified zeolite could promote the increase of the mosaicity or induce the formation of defects and cracks favorable to the diffusion of the radioactive materials, from our results radiation from ^{60}Co enhances the immobilization of the trapped cations. Furthermore, we found that cobalt γ-irradiation promotes the collapse of the zeolite framework, thereby enhancing cobalt retention. When these materials recrystallized partially, at temperatures close to 1000 °C, as nepheline, cobalt remained in the glassy amorphous material.

To reach a better understanding of the mechanisms involved in the vitrification of cobalt-exchanged zeolites and the radiation effect, a better characterization of the cobalt bonds is required. However, conventional geometrical concepts do not seem to be adequate. The surface area, for instance, is not clearly defined as there is an “external” surface area (small and determined by the area of the faces of the zeolite crystals) and an “internal” surface area (large, and due to the channels and cavities in the zeolite). Conventionally, the surface area is measured by gas adsorption (BET) or small-angle X-ray scattering (SAXS). The two techniques are complementary as, in zeolites, SAXS measures the external surface and gas adsorption measures the internal surface area. If a porous glass is under investigation, gas adsorption will not detect closed pores or bubbles.

Furthermore, depending on the gas chosen, the surface area turns out to be different by several orders of magnitude. This is the principle lying behind fractal geometry.[5] Among the methods for determining the fractal dimension, gas adsorption and SAXS are the most frequently used[6−9] in a wide range of problems. The comparison of these two techniques has been very fruitful in the characterization of densified SiO_2.[6,7]

The geometry of a system is often the determining factor in the reaction behavior of the system. In this study, we use the fractal geometry approach to characterize the effect of thermal treatment and radioactive irradiation on the cobalt environment in zeolitic materials. Small-angle X-ray scattering is utilized to determine the fractal dimension of the material, and infrared

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(1) Kalló, D. In Bish, D. L., Ming, D. W., Eds. *Application of Natural Zeolites in Water and Wastewater Treatments*, Vol. 45: The Mineralogical Society of America: Washington, DC, 2001; p 519.

(2) Földesová, M.; Lukác, P.; Majling, J.; Tomková, V. *J. Radioanal. Nucl. Chem. Lett.* **1996**, *293*, 212.

(3) Dyer, A.; Abou-Jamous, J. K. *J. Radioanal. Nucl. Chem.* **1997**, *59*, 224.

(4) Bulbulian, S.; Bosch, P. *J. Nucl. Mater.* **2001**, *64*, 295.

(5) Harrison, A. *Fractals in Chemistry*; Oxford University Press: New York, 1995; pp 49−60 and 63−65.

(6) Dieudonné, Ph.; Hafidi Alaoui, A.; Delord, P.; Phalippou, J. *J. Non-Cryst. Solids* **2000**, *155*, 262.

(7) Dieudonné, Ph.; Phalippou, J. *J. Sol−Gel Sci. Technol.* **1999**, *14*, 249.

(8) Pfeifer, P.; Avnir, D.; Farin, D. *J. Stat. Phys.* **1984**, *36*, 699.

(9) Gouyet, J. F. *Physics and Fractal Structures*; Springer-Verlag: Berlin, 1996.

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spectroscopy (FTIR) is used to understand the cobalt environment in the crystalline or glassy network. For this purpose, we have selected some of the samples prepared in our previous work. The criterion was to follow and determine the differences between the retention of cobalt by zeolite A or X as well as in the obtained glassy materials, γ-irradiated and non-irradiated and to interpret it in a fractal geometry frame.

Materials and Methods

Materials. Powdered A and X zeolites in the Na^+ form with the compositions $Na_{12}Si_{12}Al_{12}O_{48}\cdot xH_2O$ and $Na_{86}Si_{106}Al_{86}O_{384}\cdot xH_2O$, respectively, referred to as AZ and XZ were used to prepare the cobalt-exchanged zeolites mentioned in the previous paper.[4] The cobalt content of the samples was low: 0.93 and 0.83 meq/g for Co-exchanged AZ (CoAZ) and XZ (CoXZ), respectively, to prevent the desorption of cobalt ($^{60}Co^{2+}$) from the solid in the absence of external agents. The CoAZ and CoXZ samples were heated at 400, 600, 700, 800, 900, and 1000 °C, and some samples were γ-irradiated in a ^{60}Co γ-beam at 1 or 6 MGy.

Small-Angle X-ray Scattering. The powdered dehydrated samples were introduced into a capillary tube. A Kratky camera coupled to a copper anode X-ray tube was used. The data were collected with a proportional linear counter and analyzed as reported by Glatter's ITP92 program.[10−12] From the slope of the plot of the logarithm of the corrected intensity, log $I(h)$, versus the logarithm of the angular parameter, log h, where $h = 4\pi \sin \theta/\lambda$ with θ defined as the scattering angle and λ as the wavelength, the fractal dimension (D_f) was obtained. As the scattering centers in our samples are present in a relatively low concentration, single scattering predominates and the well-developed theory can thus be applied.[13] The scattering centers are all inhomogeneities present in the samples, such as alumina in the zeolites or pores in the amorphous material.

Infrared Spectroscopy. Infrared spectra of the samples (CsI waffles) were recorded in the range 4000−220 cm^{-1} using a Perkin-Elmer FTIR 2000 IR spectrometer. A detector FR-DTGS Mid-IR (CsI) was used.

Results

In our previous study,[4] the crystallinity of cobalt-exchanged zeolite A, as determined by X-ray diffraction, was maintained and the cell parameter was not altered within the range of experimental error. If the CoAZ sample was treated at 600 °C and irradiated at 6 MGy the cell parameter increased, although the crystallinity was maintained and no apparent variations of the X-ray pattern were observed. To simulate the action of seawater, a NaCl solution (1 N) was prepared and the amount of cobalt released was measured.

The plot log $I(h)$ vs log h provides the fractal dimension of the studied sample. Figure 1 compares the curves obtained for zeolites X, A, and CoAZ. The corresponding fractal dimensions for zeolites A and X are 2.20 and 1.57, respectively (Table 1). The fractal dimension of zeolite A increases from 2.20 to 2.30 when the sample is exchanged with cobalt. This exchange increases fractal dimension in both zeolites as it turns out to be 1.57 and 1.80 in zeolite X in nonexchanged and Co-exchanged samples, respectively. However, when the cobalt-exchanged zeolite A, CoAZ, was treated at 600 °C and γ-irradiated at 6 MGy the resulting fractal dimension was 2.70. Although by X-ray diffraction the three samples of zeolite A (non-exchanged, Co-exchanged, and treated) were similar (only subtle variations in the cell parameters were observed[4]) they can be distinguished by their fractal dimension (D_f).

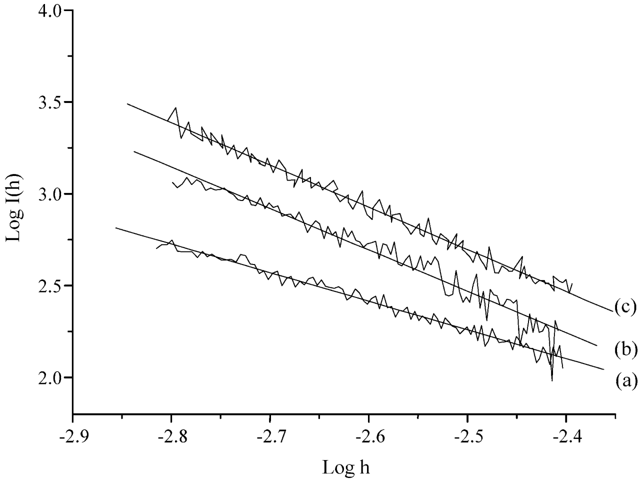

Figure 1. SAXS curves to obtain the fractal dimension of (a) zeolite X, (b) zeolite A, and (c) CoAZ.

Samples treated at 800 °C and 6 MGy were glassy materials: CoAZ became a glass and carnegeite and CoXZ was only glass as determined by X-ray diffraction, no cobalt leached from any of these materials. Their respective fractal dimensions were 2.71 and 2.11. Such values reproduce the measurements obtained in samples treated at 600 °C and γ-irradiated at 6 MGy which were crystalline materials and permitted cobalt to leach.

Figure 2 compares the infrared spectra of the non-γ-irradiated CoXZ samples. The band at 368 cm^{-1} is clearly resolved in samples treated at 700 and 800 °C showing that even at 800 °C small zeolitic entities are present.[15,16] The band close to 370 cm^{-1} was assigned by Flanigen et al.[17] to pore-opening of external linkages. However, this assignment is still under discussion in the open literature. Recently,[18,19] theoretical studies have suggested that this vibration could be a manifestation of the 4R opening vibration. From these assignments[17−19] it follows that, if this vibration is observed, zeolite entities are present. In the sample treated at 900 °C, the band at 368 cm^{-1} is not apparent and the band assigned to 6R pore opening vibration[18] is observed at 295 cm^{-1}. On the other hand, it is well-known that the paramagnetic Co^{2+} cations in partially exchanged faujasites occupy sites I′ and II′.[14,20] In these sites, the cation is near 3 ring 6R. Then, the modifications of the band at 298 cm^{-1} could be altered by modifications of the cobalt site. The 6R pore-opening motion fades and shifts as temperature is increased (Figure 2). When samples were irradiated at 1 MGy (Figures 3 and 4) even at 800 °C the band at 368 cm^{-1}

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(10) Glatter, O. *J. Appl. Crystallogr.* **1981**, *14*, 101.

(11) Glatter, O. *J. Appl. Crystallogr.* **1984**, *17*, 435.

(12) Glatter, O. *Prog. Colloid Polym. Sci.* **1991**, *84*, 46.

(13) Guinier, A.; Fournet, G. *Small-Angle Scattering of X-rays*; John Wiley & Sons: New York, 1955.

(14) Solache, M.; Garcia, I.; Bosch, P.; Bulbulian, S.; Blumenfeld, A.; Fripiat, J. *J. Microporous Mesoporous Mater.* **1998**, *21*, 19.

(15) Breck, D. W. *Zeolite Molecular Sieves*; Wiley & Sons: New York, 1974; p 418.

(16) Heilbron, M. A.; Vickerman, J. C. *J. Catal.* **1974**, *33*, 434.

(17) Flaningen, E. M.; Khatami, H.; Szymanski, H. A. *Adv. Chem. Ser.* **1971**, *101*, 201.

(18) Bornhauser, P.; Calzaferri, G. *J. Phys. Chem.* **1996**, *100*, 2035.

(19) Smirnov, K. S.; Bougeard, D. *Catal. Today* **2001**, *70*, 243.

(20) Han, J. D.; Woo, S. I. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 145.

Table 1. Small-Angle X-ray Scattering Results Compared to the Leaching Amounts of CoXZ and CoAZ

sample	γ-irradiation and thermal treatment	fractal dimension determined by SAXS	X-ray diffraction and Co leaching (previous work)
zeolite A	non-irradiated	2.20	100% crystalline zeolite A
CoAZ	non-irradiated	2.30	100% crystalline; Co leaching 25%
CoAZ	γ-irradiation at 6 MGy and treated at 600 °C	2.70	100% crystalline; Co leaching 10%
CoAZ	γ-irradiation at 6 MGy and treated at 800 °C	2.71	Glass + carnegeite; Co leaching 0%
zeolite X	non-irradiated	1.57	100% crystalline zeolite X
CoXZ	non-irradiated	1.80	100% crystalline; Co leaching 55%
CoXZ	γ-irradiation at 6 MGy	2.10	100% crystalline; Co leaching 35%
CoXZ	γ-irradiation at 6 MGy and treated at 800 °C	2.11	glass; Co leaching: 0%

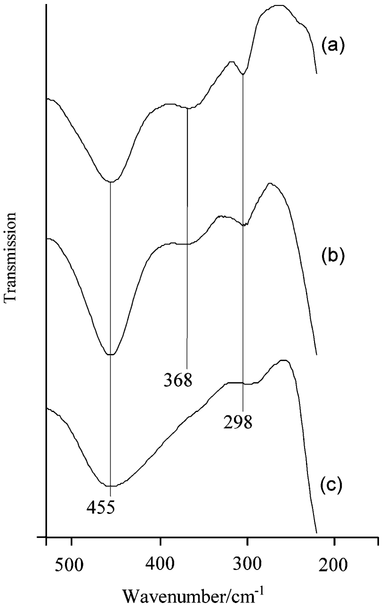

Figure 2. Infrared spectra of calcined CoXZ: (a) 700, (b) 800, and (c) 900 °C.

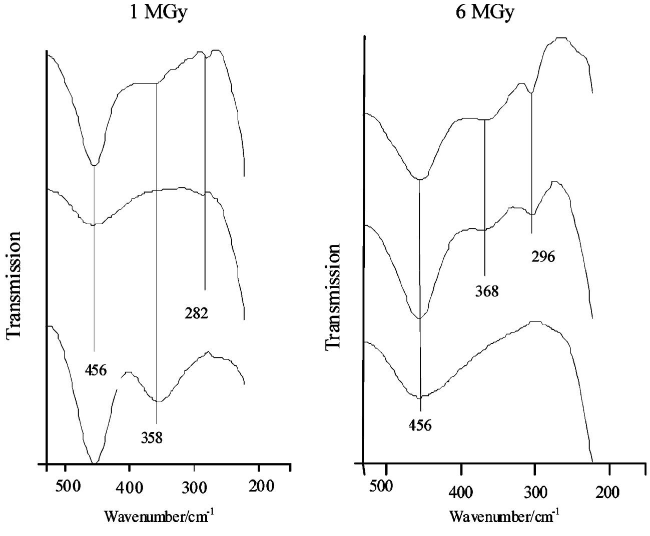

Figure 3. Infrared spectra of γ-irradiated (1 Mgy and 6 MGy) CoXZ calcined at (a) 600, (b) 700, and (c) 800 °C.

is observed, and as temperature increases the band at 298 cm^{-1} is shifted and diminishes. Finally, in samples γ-irradiated at 6 MGy (Figures 3 and 4) at 800 °C the pore-opening bands are still present and 6R pore-opening vibration becomes undefined and tends to shift to smaller values, probably as a consequence of aluminum elimination from the framework and also due to formation of paramagnetic centers when the samples are irradiated and heated.[21,22] The spectrum of the CoXZ sample γ-irradiated at 6 MGy and treated at 900 °C is most interesting, as no pore-opening band is detected and the 6R pore-opening band disappears. The cobalt site, thus, in this material, is strongly modified in such a way that no 6R pore-opening vibration is allowed. However, in the 650−750 cm^{-1} region (spectra not shown), no new bands are observed, indicating, as expected, that cobalt oxides (i.e., Co_2O_3 among others) are not formed.[23]

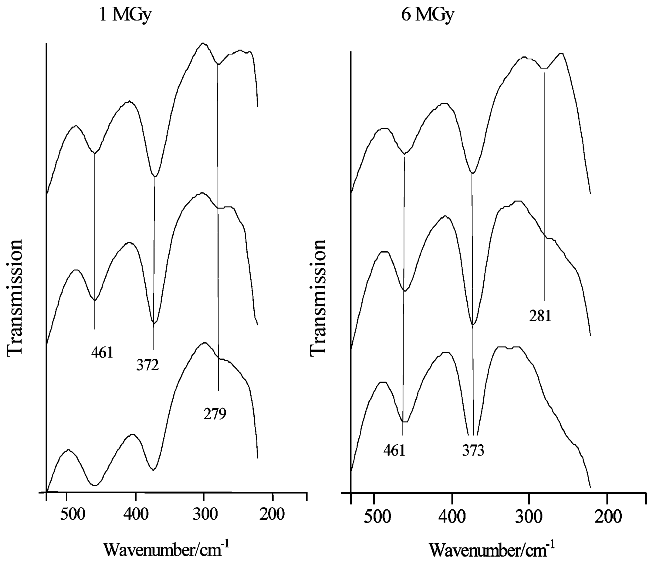

Figure 4. Infrared spectra of γ-irradiated (1 MGy and 6 MGy) CoAZ calcined at (a) 700, (b) 800, and (c) 900 °C.

Discussion

In Euclidean geometry, the dimension of an object can be defined as the minimum number of coordinates necessary to specify the position of a point contained in that object. Therefore, to define a position of a point on a line one axis is required, but two coordinates are needed to specify a position in a plane, and three are needed for a position in a volume. However, surfaces clearly exist in a three-dimensional world; they have

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(21) Decanter, J. P. M.; Maxwell, D. E. R.; Trotter, J. J. *Chem. Soc.* **1972**, 733.

(22) Vedrine, J. C.; Naccache, C. *J. Phys. Chem.* **1973**, *77*, 1606.

(23) Ng, K. Y. S.; Gulari, E. *J. Catal.* **1985**, *92*, 340.

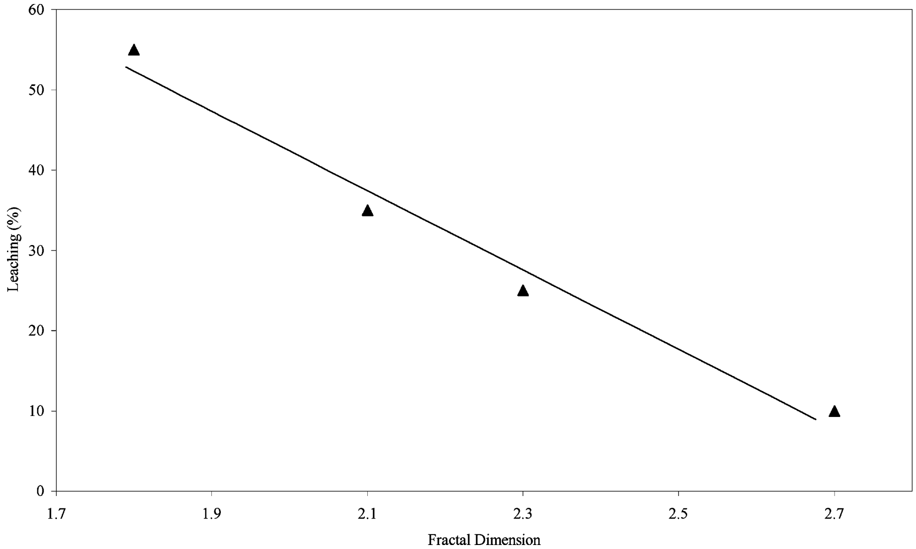

Figure 5. Correlation between fractal dimension and cobalt leaching: ◆, CoXZ; and ▲, CoAZ.

length, breadth, and depth, there are indeed foams and sponges. Fractal dimensions then reflect this situation: if the surface tends to a flat plane the fractal dimension will be very close to two, but if it is very folded it will tend to 3. Zeolites are objects which are almost only surface, they are “all bone and no flesh”. In this sense, the values of fractal dimension obtained for zeolite A and zeolite X show that as zeolite X is more open and less perfect, the fractal dimension is lower.

The fractal dimension values obtained in this work and which are very different, reflect the degree of imperfection of the two zeolites, which depends on the presence of defects, detrital alumina, or other compounds. Cobalt species reduce the connectivity of the lattice-obstructing channels and cavities. Cobalt, indeed, constitutes large $Co(H_2O)_6^{2+}$ ionic species distributed inhomogeneously in the zeolite network.[14] Still, the knowledge of the fractal dimension is insufficient to fully characterize the geometry of the sample, but it can be related to the diffusion properties. As shown by our results, the larger the fractal dimension, the lower the Co-leaching was observed (Table 1). The tendency in Figure 5, straight line or some kind of exponential law, shows that if the fractal dimension tends to 3, the leaching tends to zero. This extreme situation means that a cobalt aluminate without defects would not leach at all as all cations are occluded into the oxygen network and are not accessible to the NaCl solution.

Zeolite X fractal dimension values reproduce the tendencies found for zeolite A. The fractal dimension of the non-irradiated samples is higher than the value for the Co-exchanged sample which is also lower than the value for thermally treated (600 °C) and γ-irradiated cobalt-exchanged zeolite. In the same way, the highest the fractal dimension, the lowest the leaching value.

In Figure 5 we show that such law is independent of the zeolite structure and a clear correlation can be established in this sense. With γ-irradiation, local damage is expected because of free radicals generated by the irradiation. Loss of short-range order should obstruct the easy diffusion of cobalt atoms. Zeolite A and zeolite X channels are large. It is, then, the defects and the perfection degree of the lattice, not the structure of the channels, which determine the leaching behavior.

As cobalt does not escape from solids treated at 800 °C and 6 MGy, a different bonding to the aluminosilicate network is expected. Of course, the crystalline lattice has collapsed, but a defective and vitreous network has been formed whose apparent connectivity can be compared to zeolite connectivity. Therefore, cobalt is retained not so much becausof occlusion but because of a different bonding between the aluminosilicate and cobalt. In this sense, infrared spectroscopy results are most relevant as they are able to reveal the presence, on one hand, of cobalt interacting with zeolite network, and, on the other hand, of zeolitic pore openings independent of the crystalline long range order. The local lattice modifications proposed to interpret the SAXS result discussion are in agreement with the infrared measurements. Then, the following model emerges. The crystalline zeolite network retains cobalt and its leaching depends on the fractal dimension of the obtained solid. With temperature and irradiation, the structure of the cobalt sites is modified; as the zeolite network collapses cobalt leaching diminishes. Cobalt atoms are occluded in the glassy material and the small zeolite entities are not cobalt loaded.

Conclusion

The measurement of the fractal dimension in Co-exchanged zeolites A and X treated at various temperatures and irradiated at 1 or 6 MGy, all crystalline, showed that the lower the fractal dimension value, the higher the leaching. However, when the zeolite structure collapses the environment of cobalt changes and this correlation is no longer valid. Increasing temperature and γ-irradiation destroy selectively the zeolitic sites where the cobalt is located: the 6R pore-opening vibration is no longer observed. Cobalt sorption weakens the bonds present in the zeolite, and with temperature and irradiation these are the zones that collapse first. The remaining small crystalline zeolite particles embedded in the amorphous network do not contain cobalt, hence cobalt-exchanged zones seem to be less stable to temperature and γ-radiation than those which have retained sodium. For small adsorbed cations, chemistry of zeolites becomes a problem of local surface physics.

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