

EFFECTS OF γ -IRRADIATION ON THERMAL AND TEXTURAL PROPERTIES OF Na-Y ZEOLITES

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(Received 23 June 1986)

ABSTRACT

Na-Y zeolite specimens were subjected to different doses of γ -irradiation varying between 7 and 100 Mrad. The effect of this treatment on the structure, thermal stability and adsorption characteristics of zeolite was investigated. The techniques employed were TG, DTA, X-ray diffraction and adsorption of carbon dioxide at 25°C and nitrogen at -196°C.

The results obtained revealed that, γ -irradiation up to 100 Mrad did not lead to any appreciable change in the structure and thermal stability of the irradiated zeolite samples. However, the water content and course of its departure during thermal treatment is related to the dose applied.

The textural properties (micropore volume and pore size) were changed by doses ≥ 15 Mrad. Micropore volume decreases slightly by the dose while the D value which is a measure of the pore size progressively increases reaching a maximum limit (90%) at a dose of 60 Mrad then remained unchanged by increasing the dose up to 100 Mrad.

INTRODUCTION

Zeolites are commonly employed as molecular sieves [1–3] and as active catalysts for a variety of organic reactions [4–8]. The thermal stability of different types of zeolites and their surface and catalytic properties are dependent mainly on: (i) $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for one and the same type of zeolite [9–11], (ii) substitution of their sodium ions by other cations of varying sizes and valence states [9–14]; (iii) subjecting the solids to hydrothermal treatment and γ -irradiation [15,16]. These treatments might induce important changes in the structural, textural and acidic properties of the treated zeolites and also create different types of lattice defects [4–7,10,16].

The increase of silica:alumina ratio of Na-Y zeolite via partial dealumination of the solid increased its thermal stability [8,17,18] and modified its textural properties (increasing its surface area and its pore size) [8]. Gamma-irradiation of H-Y zeolite effected a considerable increase in its

catalytic activity for the D_2 - H_2 exchange reaction due to creation of some skeletal lattice defects [16]. Also, γ -irradiation much increased the concentration of Lewis acid sites in NaH-Y zeolites [15]. The effect of γ -irradiation on textural properties of zeolites received less attention.

The present investigation is devoted to the study of the effect of γ -irradiation on structural, textural and thermal properties of Na-Y zeolites.

EXPERIMENTAL

Materials

The sodium form of synthetic Y faujasite was obtained from Union Carbide Corporation with the designation SK-40 molecular sieve type Y.

Techniques

Na-Y zeolite samples were subjected to γ -irradiation using a ^{60}Co source. The doses were 7, 15, 30, 60 and 100 Mrad with a rate of 27 rad s^{-1} . The irradiated solids were left 3 weeks before carrying out the different measurements.

The structure of various irradiated solids was determined from X-ray diffraction patterns obtained with a Philips diffractometer (type PW 1390). The patterns were run with nickel-filtered copper radiation, $\lambda = 1.5405 \text{ \AA}$ at 40 kV and 25 mA with a scanning speed of 2° in $2\theta \text{ min}^{-1}$.

DTA and TG analyses of various irradiated solids were carried out using a thermal analyzer (Shimadzu, Kyoto, Japan). The rate of heating was kept at $15^\circ\text{C min}^{-1}$ and the sensitivity was $0.5^\circ\text{C min}^{-1}$. A 25 mg sample of each solid specimen was employed in each case.

The adsorption of carbon dioxide at 25°C and nitrogen at -196°C were determined by means of conventional volumetric apparatus under a reduced pressure of 10^{-5} Torr. Before carrying out the measurements the samples were degassed at 200°C for 3 h.

RESULTS AND DISCUSSION

X-ray diffraction of different irradiated zeolites

Figure 1 represents X-ray diffractograms of unirradiated zeolite samples and those subjected to different doses of γ -irradiation. It can be observed that Na-Y zeolite exhibits an excellent crystallinity which remained almost unchanged by γ -irradiation up to a dose of 100 Mrad. This result indicates clearly that the employed solid is characterized with a rigid and stable

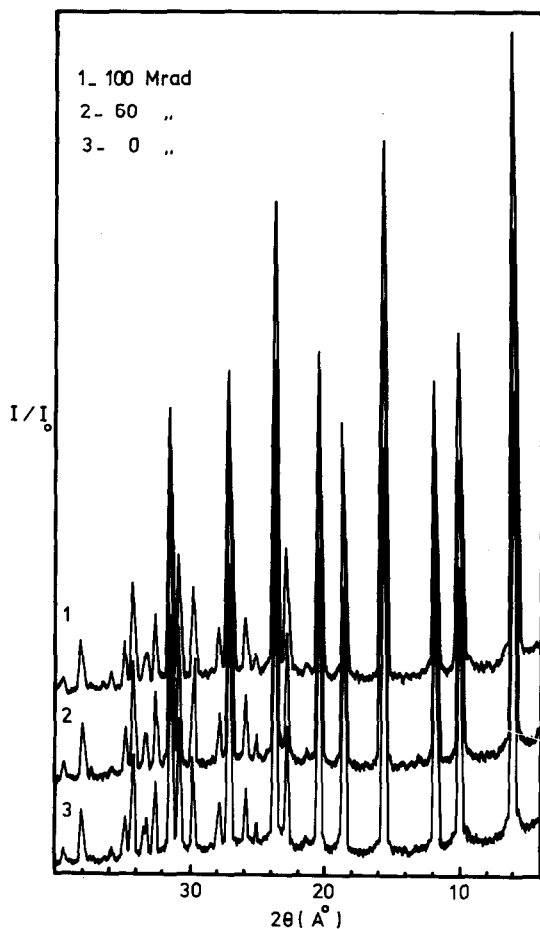


Fig. 1. X-ray diffraction patterns of unirradiated zeolite specimen and those subjected to different doses of γ -irradiation.

structure resisting the irradiation process. The same conclusion has been reached by removing about 40% of the framework aluminium in Na-Y zeolite without changing its structure as indicated by X-ray diffraction patterns of dealuminated zeolites [8,17,18].

Thermal decomposition of various irradiated solids

Figure 2 (a and b) represents DTA and TG curves of unirradiated and different γ -irradiated zeolites. One strong and sharp endothermic peak at 60–200°C, with its maximum located at 100°C, is observed in all cases. The area of this peak increases by increasing the dose up to 60 Mrad then decreases at a dose of 100 Mrad. One weak exothermic peak at about 1000°C is detected for all solids. The endothermic peaks were followed by

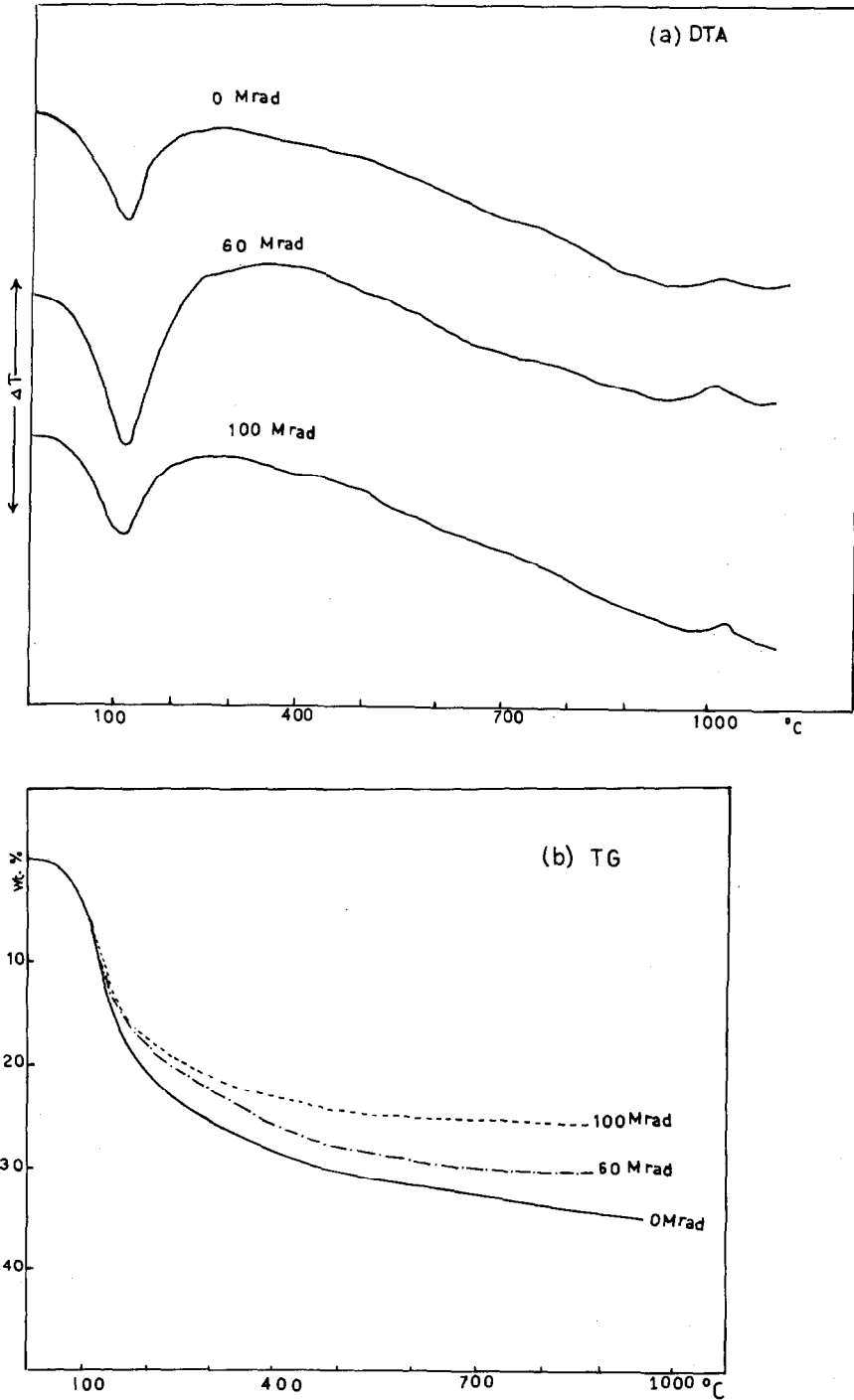


Fig. 2. DTA and TG curves of unirradiated and γ -irradiated zeolite specimens.

weight losses of 18, 18 and 12% for unirradiated, 60 and 100 Mrad irradiated zeolite samples, respectively, while the exothermic peaks were not accompanied by any change in weight. The total loss in weight attained 36, 31 and 27% in the case of unirradiated samples and those subjected to 60 and 100 Mrad, respectively. The loss in weight at temperatures ranges between 450–850°C reached 4, 2 and 2% for unirradiated, 60 and 100 Mrad irradiated solids, respectively. The endothermic peaks at 60–200°C indicate the departure of weakly bound water molecules of zeolite, while the loss in weight occurring at temperatures in the range 450–850°C might correspond to a dehydroxylation process (departure of structural OH groups of zeolite). The exothermic peaks at 1000°C indicated the thermal decomposition of Na–Y zeolite, i.e., transformation from a definite crystalline zeolitic structure to amorphous phases, sodium and aluminium silicates [17,18]. The fact that γ -irradiation decreased the total loss in weight and that taking place at 450–850°C, to an extent proportional to the dose employed, indicated that the energy of γ -rays absorbed by the zeolite sample caused the departure of some of its water content and enhanced the dehydroxylation process during thermal treatment of the irradiated solid. It can thus be concluded that γ -irradiation up to 100 Mrad did not exert any detectable effect on the thermal stability of Na–Y zeolite. However, the water content and course of its departure during thermal treatment was effectively modified by γ -irradiation.

It is well known that the water content of zeolites much affects their catalytic activities [4,7] and may induce some changes in their textural properties. The textural characteristics of zeolites, namely surface area, micropore volume and pore size, are usually determined from nitrogen and carbon dioxide adsorption isotherms.

Adsorption of nitrogen and carbon dioxide on unirradiated and different irradiated zeolite specimens

Preliminary experiments showed that the adsorption of nitrogen at -196°C on the unirradiated and 100 Mrad irradiated solids exhibited one and the same isotherm. This indicates that γ -irradiation does not lead to any appreciable change in nitrogen adsorption capacity. The adsorption isotherm of nitrogen on both samples, not given in the text, is very steep at the initial low relative pressure range followed by a horizontal part covering a wide range of relative vapour pressure (0.05–0.9). The BET equation is thus not convenient in the case of such isotherms and its application is not expected to give a significant measure of the surface area. In fact, it is well documented that CO_2 adsorption at 25°C is the most suitable adsorbate for determining the surface area of microporous carbons and zeolites [19,20].

The adsorption of CO_2 at 25°C was measured on the original and γ -irradiated zeolites. Measurements in the pressure range 15–800 Torr was

followed and an equilibrium time of 20 min was allowed between successive measurements. At 25°C, the saturation vapour pressure of CO₂ was taken as 48 300 Torr [21]. The specific surface area, micropore volume and pore size of various solids were calculated from CO₂ adsorption isotherms at 25°C by a direct application of Dubinin–Radushkwick equation in its linear form [22].

$$\log V = \log V_0 - D \log^2(P/P_0)$$

where V is the volume (cm³ g⁻¹) of carbon dioxide adsorbed at relative pressure P/P_0 , V_0 is the micropore volume and the gradient D is a measure of average pore size.

The linear D - R plots of CO₂ adsorbed on the solids investigated are shown in Fig. 3. All the adsorption points lie on a single straight line indicating that adsorption of CO₂ at 25°C can be employed satisfactorily as a convenient method of investigating the internal structure of zeolite samples.

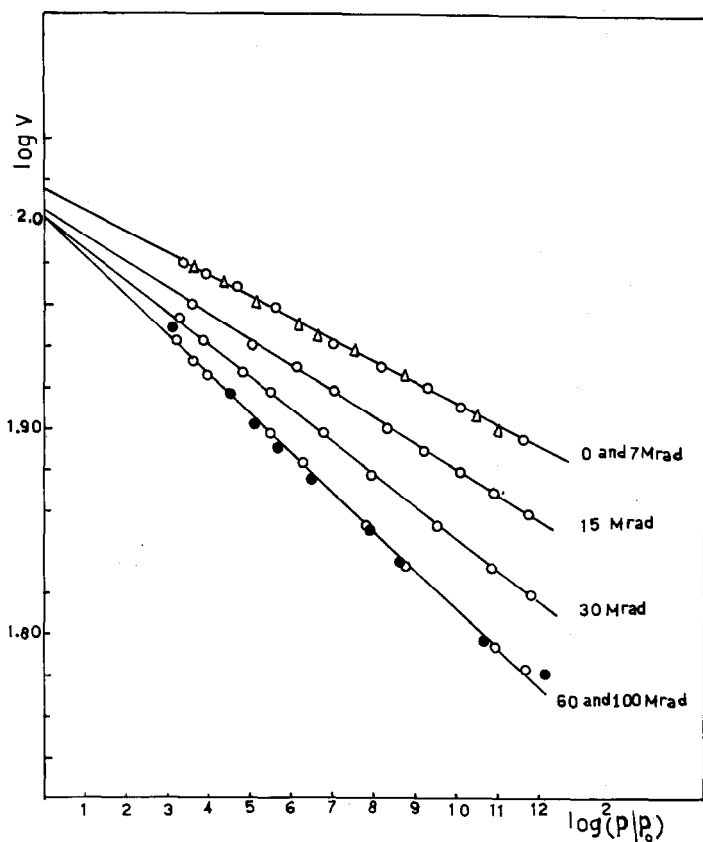


Fig. 3. D - R plots of adsorption of CO₂ at 25°C on Na-Y zeolite samples exposed to different doses of γ -radiation.

It is evident from Fig. (3) that the adsorption points of the unirradiated and 7 Mrad irradiated samples lie on the same linear $D-R$ plot. A dose as low as 7 Mrad may be considered insufficient for measurable variation either in the total micropore volume or pore size of zeolite sample.

Irradiation with higher doses leads to some significant changes in the porosity of zeolite as follows. (i) Slight decrease in the micropore volume for sample irradiated with 15 Mrad. This decrease continues with the increase of the dose to 60 Mrad, further increase in the dose does not lead to more decrease in the micropore volume. (ii) Increasing the dose from 15 to 60 Mrad is associated with continuous and regular increase in the D value. The increase in the magnitude of D attains 30, 60 and 90% for the doses of 15, 30 and 60–100 Mrad, respectively. The regular increase in the value of gradient D suggests that γ -irradiation may result in a regular increase in the average pore size of the irradiated zeolite samples. The TG investigation, presented previously, showed that γ -irradiation enhanced both the departure of water content and dehydroxylation process to an extent proportional to the dose employed. It seems that the resulting increase in the pore size of irradiated solids can be attributed to an enhanced removal of water content of zeolite (molecular H_2O and OH groups) during thermal treatment.

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