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The Solid State Reduction of Sodium Ions in NaY Zeolite by Electron Bombardment

We recently published studies on the use of low-energy electron sources to compensate for charge generated when acquiring a photoelectron spectrum of insulators (*1*). During this work we examined samples for evidence of chemical damage arising from the electron beam, as a function of beam potential. Chemical damage is only rarely observed but we report one example because of the means which it affords for the production of a potentially useful reducing agent.

A VG ESCA3 MkII X-ray photoelectron spectrometer fitted with Mg$K\alpha$ and monochromatic Ag$L\alpha$ X-ray sources was used for a study of Y-type faujasites in Na, Li, Cs, or Mg ion-exchanged forms (*2*). Monochromatic Ag$L\alpha$ X-rays were chosen for their ability to excite 1*s* photoelectrons from Al and Si. Initially low-energy flood gun electrons (<2 eV) were used to equilibrate any surface charging effects (VG LEG 51 model used), but the reproducibility of peak positions was poor, probably due to contributions from both the material and the spectrometer. In previous work (*1*) we showed that the peak separations and their reproducibilities become constant when neutralising beams of greater energy are used. Accordingly the energy of the flooding electrons was increased stepwise over the range 0–10 eV.

The electron-induced chemical changes occurred with electron beam energies >6 eV for the Na-exchanged samples while the other samples remained unaffected. The principal observation was the reduction of Na from ionic to metallic species; this was accompanied by a change in color of the specimen (pink–red–purple–black, with time) and an increase in the surface concentration of sodium (Table 1). The experiment was repeated several times.

Figure 1 gives photoelectron spectra recorded in Mg$K\alpha$ radiation. Dots represent the experimentally recorded values of photoelectron yield at 0.1-eV intervals, while the lines show the results of deconvolution of the data into constituent peaks according to an in-house peak fitting routine (*3*). The minor peak labeled Al 2$p(K\alpha_{3,4})$ is the peak due to Al 2*p* photoelectrons excited by the less intense Mg$K\alpha_{3,4}$ X-rays. Line A depicts the result prior to sample exposure to 10-eV flood gun electrons while line B shows the result following such exposure. The Al^{3+} 2*p* line at ≈75.2 eV can be seen to be almost unchanged following electron exposure, while a new line due to unoxidized sodium appears in the Na 2*s* region and the original line at 65.6 eV due to oxidized sodium is markedly reduced in intensity.

The increase in surface concentration of sodium during a study of supported catalyst systems has been observed before (*4*). However, it occurred with an electron

TABLE 1

Surface Composition Changes Recorded before and after 10-eV Flood Gun Exposure (from Spectra Using Mg$K\alpha$ Radiation)

Experiment	Atomic %				
	Na	Al	Si	O	C
Before	13.2	8.0	11.4	50.3	16.9
After	25.1	6.4	8.2	41.2	17.7

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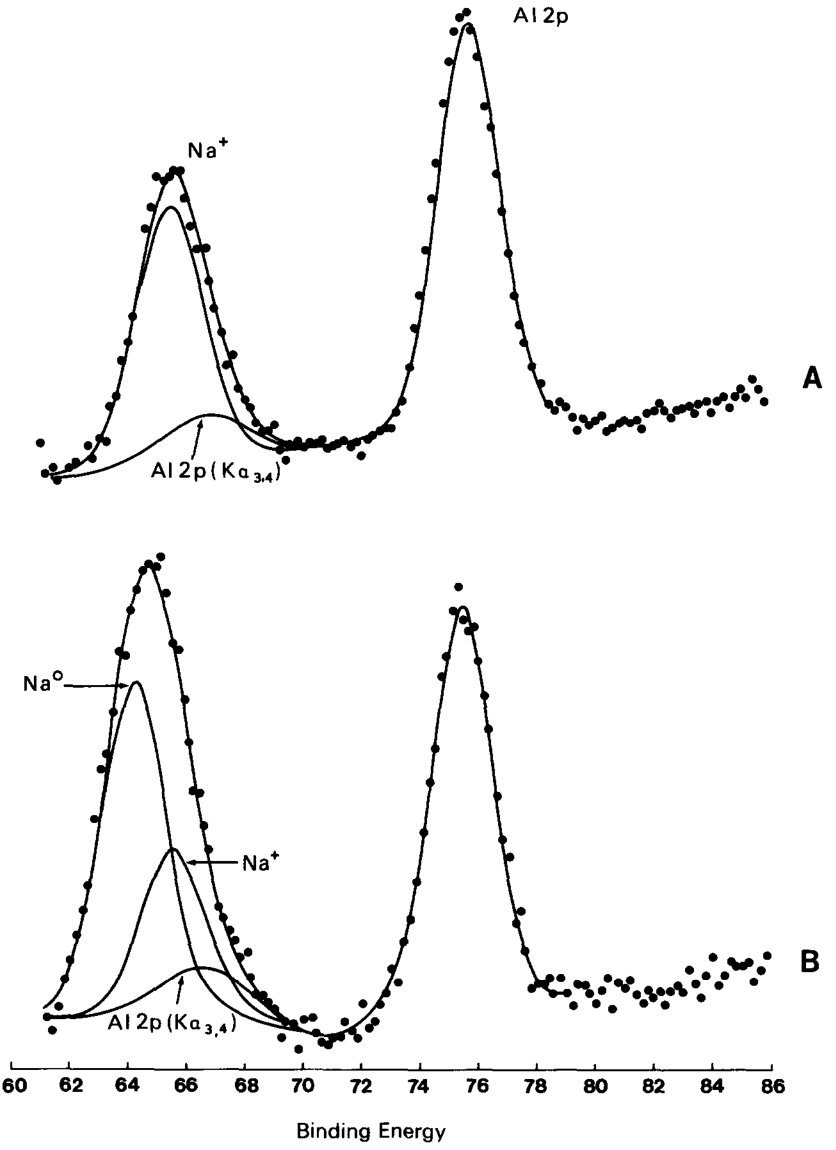

FIG. 1. X-ray excited photoelectron spectra for Na–Y zeolite, Al 2*p* and Na 2*s* region, before (A) and after (B) exposure to flood gun electrons (10-eV bias). Binding energy in electron volt units.

beam of 8000 eV and is perhaps not unexpected. The reduction reported here occurs quite specifically as the flood gun beam energy is increased from 6 to 8 eV.

The reaction

$$2Na_2O \rightarrow 4Na + O_2$$

may serve as a simplified model and is equivalent to the solid state electrochemical reduction of sodium ions to the metallic state. The free energy change is ≈8 eV under standard conditions (*5*) and this would be reduced by ≈2 eV because of the low-pressure environment and by any small increase in the temperature of the sample. This suggests that the flood gun electrons act directly to provide the free energy of reaction. The first ionisation energy for sodium is equivalent to 5.2 eV; this compares favourably with the above result and suggests that little, or no, energy is lost in penetrating the zeolite framework. Electron capture cross-sectional effects would influence the time dependence of the reaction.

We believe that the efficient production of a highly dispersed form of metallic sodium on a zeolite substrate might be of interest as a strong reducing agent.

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