

## An EPR Study on Nitrogen Monoxide Adsorbed on Sodium Ion-Exchanged A-type Zeolite

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(Received March 24, 2000; CL-000279)

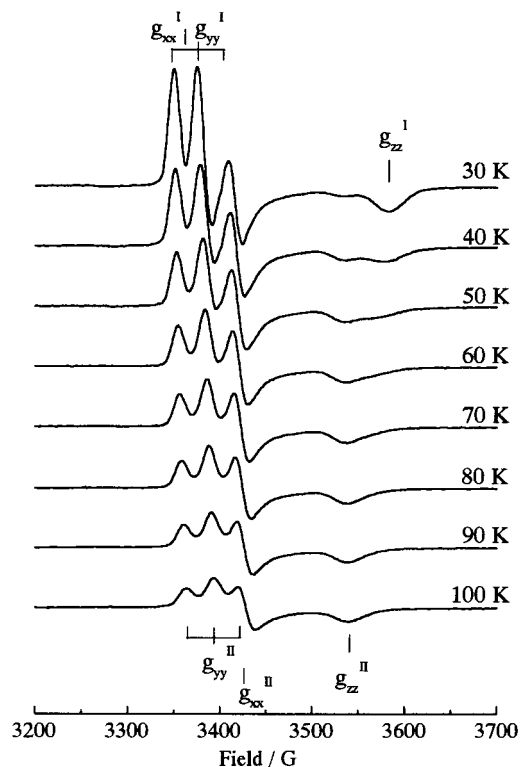
Temperature-dependent EPR spectra of nitrogen monoxide (NO) introduced into sodium ion-exchanged A-type (Na-A) zeolite demonstrated that two types of NO monoradical and one NO-NO radical pair were formed on the zeolites and that the thermally less stable NO monoradical was converted into the thermally stable one upon warming from 30 K to 100 K.

Among various spectroscopic techniques, electron paramagnetic resonance (EPR) is one of the best methods due to its sensitivity to the details of the structure of the molecule adsorbed on zeolite. Lunsford<sup>1</sup> has first reported EPR spectra of NO molecules trapped in sodium-ion exchanged Y-type zeolite (Na-Y). After this report, a number of EPR studies of NO adsorbed on zeolites were performed, e.g. for Na-A, Ca-A, Na-X, and H-mordenite,<sup>2</sup> Na-, Ba- and Zn-Y zeolites,<sup>3</sup> and H- and Na-ZSM-5,<sup>4</sup> indicating the formation of NO monoradical consisting of a single NO molecule. Kasai and Gaura<sup>5</sup> have reported the formation of a NO-NO radical pair (NO biradical) in Na-A zeolites. However, in earlier studies,<sup>1-6</sup> EPR spectra measured at a few temperatures were only analyzed; little is known about systematic changes of EPR spectra against the temperature. The temperature-dependent EPR experiments can be potentially useful to obtain information about the thermal transformation of radicals as well as their motional dynamics. Here, we wish to report on the formation of a new and thermally unstable NO monoradical on Na-A zeolite and its transformation to a stable NO monoradical through the temperature-dependent X-band EPR measurements. Low temperature-spectroscopic studies can give information about intermediate species of the catalytic reaction with a short lifetime, which have never been observed at high temperature; it can be useful as basic information to understand catalytic reaction mechanisms associated with the zeolite.

Na-A zeolites used in the present study were supplied by Tosoh Co. Prior to EPR measurements, the samples were pre-treated as follows; Na-A samples were maintained at 473 K for 1 h in air, followed by heating to 673 K in vacuum. After keeping the temperature at 673 K for 1 h, the sample was exposed to oxygen (5 kPa) in order to oxidize some organic impurities on the zeolite, evacuated for 30 min, and then cooled down to room temperature. NO (0.1 and 1.2 kPa) was added to the sample at room temperature at least for 24 h.

X-band EPR spectra were recorded with a Bruker ER-200 D spectrometer. The microwave power was adjusted to avoid saturation. The measurement temperature was controlled using a He flow cryostat. The spectral line-shape simulations of the allowed transitions were performed using the Bruker program, Simfonia.

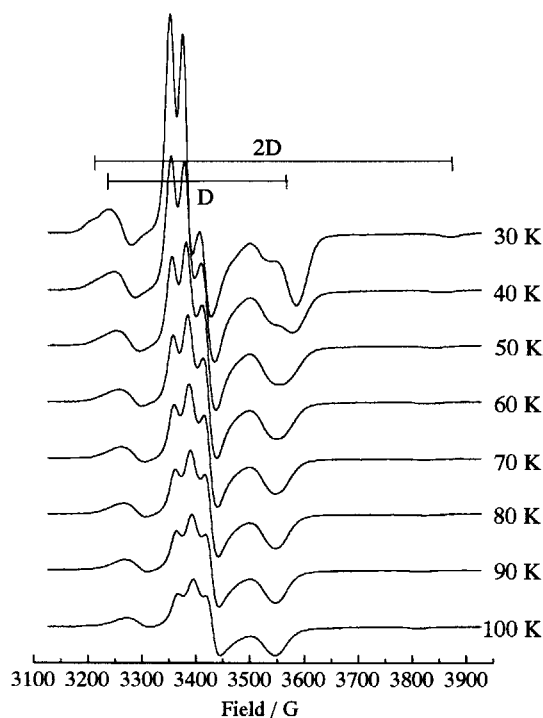
Figure 1 shows EPR spectra for NO (0.1 kPa) adsorbed on Na-A zeolites, recorded in the temperature range 30–100 K. No signal attributable to NO biradical mentioned later was detected in



**Figure 1.** X-band EPR spectra of NO (0.1 kPa) introduced into Na-A. The microwave frequency was 9.454 GHz.

these spectra because of the low NO pressure in the sample. In the previous studies of NO adsorbed on zeolites, the formation of only one type of NO monoradical with three different resolved  $g$ -tensor components and a resolved  $y$ -component of the hyperfine coupling due to the  $^{14}\text{N}$  nucleus was reported on each zeolite.<sup>1-4</sup> However, the EPR spectrum of NO adsorbed on Na-A could not be explained by only a NO monoradical. Therefore, we assumed the presence of two NO monoradicals, NO(I) and NO(II), with EPR parameters;  $g_{xx}^I = 2.002$ ,  $g_{yy}^I = 1.996$ ,  $g_{zz}^I = 1.886$ ,  $A_{xx}^I = A_{zz}^I = 0$  G, and  $A_{yy}^I = 33$  G for NO(I) and  $g_{xx}^{II} = 1.979$ ,  $g_{yy}^{II} = 1.993$ ,  $g_{zz}^{II} = 1.909$ ,  $A_{xx}^{II} = A_{zz}^{II} = 0$  G, and  $A_{yy}^{II} = 30$  G for NO(II). The sticks in Figure 1 represent the  $g$ -values of each monoradical. In the spectrum recorded at 30 K, both monoradicals were observed although the intensity of NO(I) monoradical was much stronger than that of NO(II). When the measurement temperature was increased, the signal of NO(II) monoradical became stronger, while the NO(I) monoradical gradually decreased in intensity and disappeared completely at 80 K. The spectrum above 80 K was found to be essentially the same as that of briefly evacuated NO/Na-A reported previously.<sup>5</sup> Therefore, it was concluded that

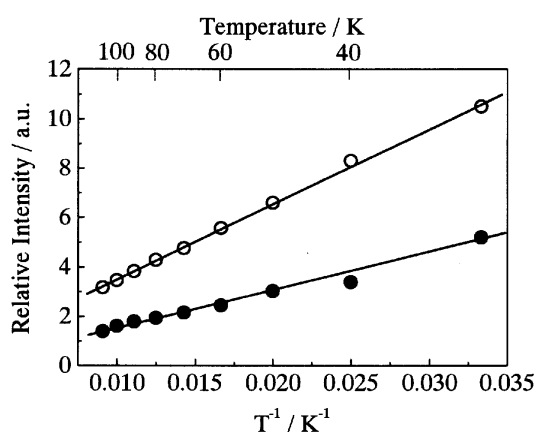
at least two types of NO monoradicals existed in NO/Na-A zeolite; one is thermally less stable NO monoradical (NO(I)) and the other is thermally stable one (NO(II)). The z-component reflects the degree of interaction between NO molecule and cation in zeolite, as derived from the energy-level diagram of NO.<sup>6</sup> In the present case,  $g_{zz}^{\text{II}}$  was larger than  $g_{zz}^{\text{I}}$ . This result suggests that NO(II) is more strongly adsorbed on  $\text{Na}^+$  ion in zeolite than NO(I).



**Figure 2.** X-band EPR spectra of NO (1.2 kPa) introduced into Na-A. The microwave frequency was 9.456 GHz.

With the increment of NO pressure, in addition to the signal of NO monoradicals mentioned above, the signal of a biradical was detected. Figure 2 shows EPR spectra for NO (1.2 kPa)/Na-A samples, recorded in the temperature range 30–100 K. The signal of a biradical possessing both anisotropic  $g$ - and zero-field splitting tensors ( $g_{xx} \approx g_{yy} \approx 1.98$ ,  $g_{zz} \approx 1.91$ , and  $D \approx 333$  G), was observed at 30 K (represented by sticks in Figure 2). With the increment of temperature, the overall signal features of the biradical were not changed; however, the  $D$  splitting became smaller with temperature. This suggests that the inter-radical distance increases with temperature.

Figure 3 shows the relationship between the signal intensity evaluated from the spectra shown in Figures 1 and 2 and the measurement temperature. The signal intensities were determined by numerical double integration of the first-derivative spectra, where the interval of integration was 3300–3700 G and 3150–3920 G for the spectra in Figures 1 and 2, respectively. Interestingly, the observed signal intensities of the spectra in Figure 1 obeyed the Curie law of paramagnetism (represented by the solid lines in Figure 3) in the entire temperature region tested in the present study, 30–100 K, indicating that, even if the intensity ratio of two NO monoradicals was changed, the total radical concentration remained constant. This result clearly shows that



**Figure 3.** Temperature dependences of the EPR double integral intensity evaluated from the spectra shown in Figure 1 (open circles) and Figure 2 (closed circles). The solid lines indicate the paramagnetic Curie law.

the thermally less stable NO monoradical, NO(I), is changed into the stable one, NO(II), without decay. The detailed transformation mechanism is not clear yet, but some conclusions can be drawn from the present results. One may assume that both NO monoradicals are adsorbed on sodium ions in the course of rapid cooling to 30 K. With increasing temperature NO(I) becomes mobile due to the rotational and/or translational diffusion motion so that NO(I) reorients to a more thermally stable position on the same sodium or migrates to another sodium to form stable NO(II).

The signal intensities of the spectra shown in Figure 2 followed the paramagnetic Curie law, indicating no change in the radical concentration between 30–100 K. Assuming that the total radical concentration of the NO monoradicals remains constant in the temperature range 30–100 K even at higher NO pressure, the radical concentration of biradical should also remain constant.

In conclusion, the temperature dependent X-band EPR study for NO adsorbed on Na-A zeolite demonstrated that at least three different kinds of EPR active forms of NO, one biradical and two monoradicals, were formed in the Na-A zeolite and that the total concentration of these radicals was independent of the measurement temperature. Further study on the location and the geometrical structure of these radicals are in progress.

The present study was partially supported by grants from the Swedish Foundation for International Cooperation in Research and Higher Education (STINT) and Saneyoshi Foundation. N.P.B. was financed by a stipend from KVA (Royal Swedish Academy of Sciences) and JSPS (The Japanese Society for the Promotion in Science).

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