FACILE REDUCTION OF CARBON MONOXIDE IN ZEOLITES BY IONIC SODIUM CLUSTERS

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Received 20 April 1988

Ionic alkali clusters such as Na_4^{3+} produced as (dark purple) zeolites under mild conditions efficiently activate carbon monoxide even at −130 °C. The well-resolved ESR spectra showing both ^{23}Na and ^{13}C hyperfine splittings provide structural insight into the initial CO interaction.

1. Introduction

Addition of alkali metal promoters such as sodium and potassium is known to be effective in Fischer-Tropsch synthesis [1]. Such an activation of carbon monoxide can occur via reactive metalcarbonyl species in homogeneous [2] and heterogeneous [1,3] catalytic processes, or also by direct reductions with alkali metals [4], thermally activated basic metal oxides [5], and electrochemical methods [6]. Indeed it was earlier suggested that ionic alkali clusters should exhibit interesting catalytic properties when they are immobilized in zeolites [7]. However an attempt to activate carbon monoxide with stable ionic sodium clusters such as Na_4^{3+} in zeolite Y was unsuccessful [8].

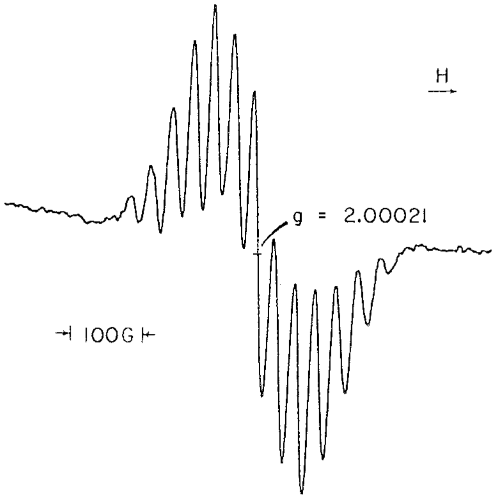

Fig. 1. ESR spectrum of Na_4^{3+} in zeolite X at 25 °C.

We recently found an efficient and selective method for the synthesis of metastable ionic sodium clusters by the liquid phase treatment of zeolites with organolithium reducing agents at ambient temperatures [9]. The facile formation of Na_4^{3+} clusters in zeolite X is illustrated in fig. 1 by the clean 13-line ESR spectrum at $\langle g \rangle = 2.0030$ with hyperfine splittings of 29 gauss due to four equivalent sodium nuclei $[I(^{23}Na) = 3/2]$. It is singularly noteworthy that a central line at $\langle g \rangle = 2.0024$ due to sodium aggregates (Na_x) is absent, and it distinguishes this method from those previously employed at high temperatures ($> 300\,°C$) such as sodium metal evaporation or controlled thermolysis of sodium azide impregnated in zeolites [7,8,10]. Indeed our Na_4^{3+} clusters are thermally labile–the dark purple zeolite being bleached when heated at 120 ° C under an argon atmosphere and its ESR spectrum was then dominated by the sharp singlet of Na_x at $\langle g \rangle = 2.0024$.

2. Experimental

2.1. SYNTHESIS OF IONIC SODIUM CLUSTERS IN ZEOLITE X

Zeolite X (Strem Chemical, 10 g of Lot No. 120370) was stirred with cobalt(II) acetate (150 mg) dissolved in 1 L of distilled water, dried at 90 ° C overnight, and activated by slowly raising the temperature of the contents of an evacuated flask ($< 10^{-5}$ torr) up to 450 ° C over the course of 6 hr. Without exposure to air, the pale blue zeolite was treated with 15 mL of a 1 M solution of n-butyl-lithium in hexane (Aldrich), whereupon it immediately turned purple. After 48 hrs, the dark purple zeolite was washed repeatedly with fresh hexane under an argon atmosphere and finally dried in vacuo. This Na_4^{3+} cluster will be hereafter referred to simply as purple zeolite. The presence of cobalt appeared to facilitate the sodium reduction since an untreated (colorless) sample of zeolite X turned dark purple more slowly after exposure to n-BuLi. Furthermore the ESR spectrum of the purple zeolite prepared in the absence of cobalt catalysis differed from that in fig. 1 in that it always contained an intense additional central component at $\langle g \rangle = 2.0024$.

2.2. ACTIVATION OF CARBON MONOXIDE

The exposure of carbon monoxide to the purple zeolite was carried out in evacuated Schlenk flasks that were precooled to an appropriate temperature. The uptake of CO was measured manometrically with a calibrated pressure transducer [B & F Instruments model 1-700 SG]. The ESR measurements were carried out in 5 mm suprasil quartz tubes in which the purple zeolite was loaded under an argon atmosphere (glovebox). The ESR tube was cooled to either $-78\,°C$ in a dry ice/acetone bath or $-130\,°C$ in a n-pentane slurry. Carbon monoxide was slowly introduced via the teflon-seal stopcock without contamination by air. The purple color was immediately bleached. (When purple zeolite prepared from cobalt-free Na X was used, the bleached sample was completely colorless.) The experiments with isotopically labelled carbon monoxide were carried out with 99%-enriched ^{13}CO (Monsanto Research Corp.).

2.3. SPECTROSCOPIC MEASUREMENTS

ESR spectra were recorded on a Varian E-112 X-band spectrometer with 100 kHz modulation using the perylene cation radical as the field marker with $\langle g \rangle = 2.000214$. The IR spectra of Na_4^{3+} clusters (before and after treatment with carbon monoxide) were prepared as KBr pellets in a nitrogen-filled glove box and measured on a Nicolet 10DX FT spectrometer with 2 cm^{-1} resolution. Electronic spectra were obtained on a Hewlett-Packard 8450A diode-array spectrometer.

3. Results and discussion

Purple zeolite containing Na_4^{3+} clusters reacted with carbon monoxide at $-130\,^\circ C$ as indicated by the gradual disappearance of its characteristic 13-line ESR spectrum (fig. 1) over a period of 4 hrs. This transformation was accompanied by a dramatic bleaching of the intense purple color, and the simultaneous appearance of a new ESR spectrum. At $-78\,^\circ C$, the purple zeolite was transformed immediately upon exposure to carbon monoxide. The exothermic process was apparent by the heat generated when CO was admitted at room temperature to the flask containing purple zeolite, and the surface turned yellow. The new ESR spectrum shown in fig. 2 consisted of a slightly anisotropic quartet ($a_{Na} =$ 16.5 gauss) with $\langle g \rangle = 2.0045$ [11]. When isotopically labelled carbon monoxide was used, each line of the quartet was further split by the ^{13}C nuclei ($I = 1/2$) into a 1 : 2 : 1 triplet ($a_{2C} = 11$ gauss) as indicated by the comparison with the computer simulated spectrum in fig. 3 [12]. Thus the ESR spectra in figs. 2 and 3 are consistent with a paramagnetic product containing at least one sodium and two equivalent carbon monoxide moieties. Its presence in the zeolite was also indicated by the appearance of a strong, sharp band at 1467 cm^{-1} and a relatively weak, broad band at 1610 ± 30 cm^{-1} in the infrared spectrum (fig. 4A). It is noteworthy that both bands were shifted ~ 40 cm^{-1} upon the use of the isotopic ^{13}CO (fig. 4B). Quantitative analysis revealed the uptake of 12 mL of carbon monoxide at atmospheric pressure by each gram of purple zeolite. This corresponded roughly to an equimolar stochiometric relationship if every sodalite unit in the purple zeolite were occupied by a Na_4^{3+} cluster.

The CO-treated Na_4^{3+} cluster was highly sensitive to dioxygen. Thus the colorless surface immediately turned pink and then pale yellow, simultaneous with the obliteration of the quartet splitting in the ESR spectrum (fig. 2) to yield

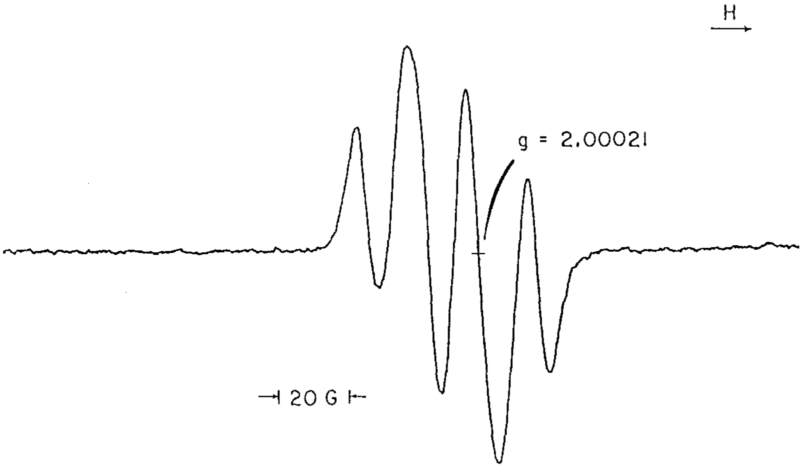

Fig. 2. ESR spectrum (25 °C) obtained from the treatment of Na_4^{3+} in zeolite X with carbon monoxide at −78 °C.

a broad, unresolved singlet at $\langle g \rangle = 2.0049$. Furthermore a weak, unresolved ^{13}C-hyperfine structure ($a \sim 16$ gauss) was observed in the ESR spectrum when dioxygen was introduced into the Na_4^{3+} cluster that was treated with isotopically labelled carbon monoxide. Dioxygen also caused the 1467 cm^{-1} band in the IR spectrum to disappear completely, and the broad, weak band intensified into a pair of distinct bands at ~ 1650 and ~ 1580 cm^{-1}.

Attempts to establish the structure of the paramagnetic product from CO and Na_4^{3+} by isolation have as yet not been successful. For example, the treatment of the bleached zeolite with anaerobic water yielded a clear, light yellow aqueous extract. Removal of water in vacuo afforded an amorphous, pale yellow solid showing a weak ESR spectrum [$\langle g \rangle = 2.0045$] with a quartet splitting ($a = 16.5$ gauss) similar to that illustrated in fig. 2. Moreover exposure of the yellow solid to dioxygen led to the same change in the ESR spectrum as that observed in the zeolite sample described above. Repeated and various attempts to separate the CO-containing product from the complex mixture have been unfruitful. However our spectral results are strongly reminiscent of the ESR spectra obtained in the previous studies of CO adsorption on thermally activated magnesium and calcium oxides [5]. For example, Morris and Klabunde [5a] obtained a series of anisotropic ESR spectra with $g_{av} = 2.0043$ showing a ^{13}C hyperfine splitting of 11.8 gauss. Their best simulation of the ESR spectra was consistent with a 2-C spin system which they assigned to a cyclic oxocarbon $C_6O_6^{3-}$ (rhodizonate) that was asymmetrically adsorbed to the surface to produce a paramagnetic semidionetype species [13]. As attractive as this proposal is, the absence of coloration in our system (at < −80 °C) indicates the formation of a less extensively delocalized oxocarbon species [14]. Furthermore the unusually large metal hyperfine splitting

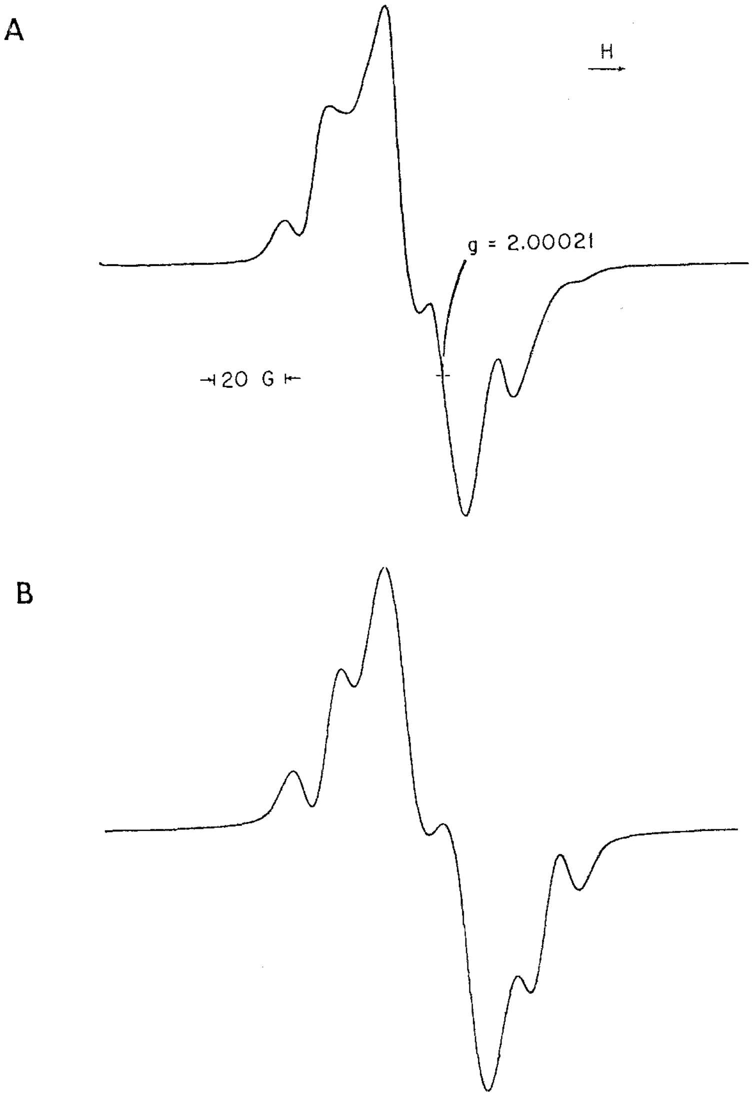

Fig. 3. (A) ESR spectrum obtained as in fig. 2 except with carbon-13 monoxide. Note broadening of the highfield line. (B) Computer simulated spectrum as described in [12].

(a_{Na} = 16.5 gauss) suggests the presence of an intimate ion-paired structure due the zeolite structure.

4. Conclusions

Success with the structural elucidation notwithstanding, we have demonstrated that ionic alkali clusters produced in the zeolite matrix under mild conditions can

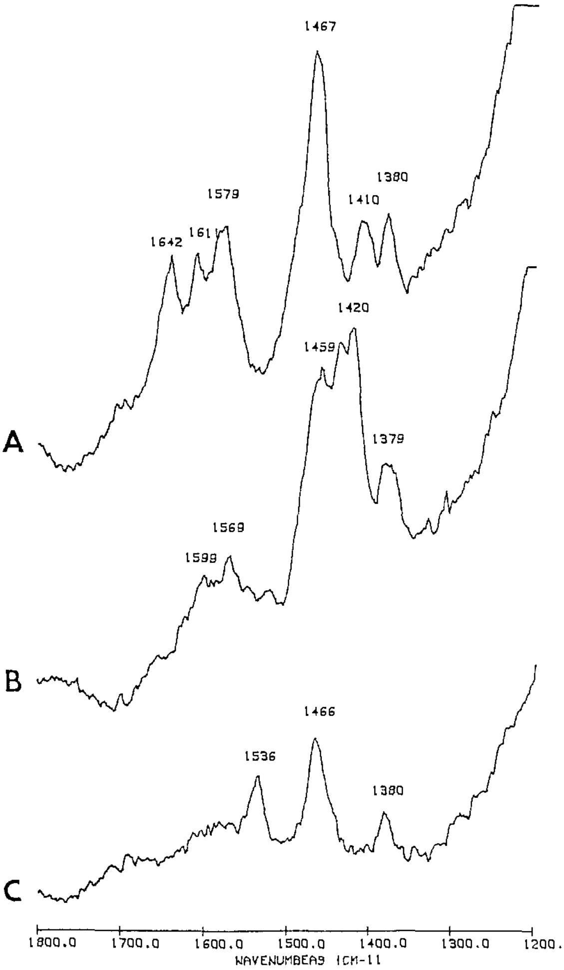

Fig. 4. Changes in the infrared spectrum attendant upon the addition of an atmosphere of carbon monoxide (A) and carbon-13 monoxide (B) to Na_4^{3+} cluster in zeolite X (C; the IR bands at 1466 and 1380 cm^{-1} are tentatively assigned to solvent impurities).

successfully activate carbon monoxide even at −130 °C. This observation contrasts with the high temperature (~ 300 °C) requirement for CO activation with bulk sodium metal [15]. Most importantly, our results strongly encourage further studies of ionic clusters in the enhancement of zeolite catalysis for reductive carbonylations.

Acknowledgements

We thank the R.A. Welch Foundation and the National Science Foundation for financial support.

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[11] The same ESR spectrum was observed with Co-free purple zeolite but the quartet shown in fig. 2 was obscured by the strong central component at $\langle g \rangle = 2.0024$ inherent in the zeolite (vide supra).

[12] For the computer simulation, the following parameters were used: $a_{\mathrm{Na}} = 16.5$ G, $a_{\mathrm{C}} = 11.2$ G with $\Delta H_{\mathrm{pp}} = 8$ G plus an underlying broad singlet with $\Delta H_{\mathrm{pp}} = 33$ G.

[13] Compare G.A. Russell and C.E. Osuch, J. Am. Chem. Soc. 104 (1982) 3353 and related papers.

[14] See for example the alkali metal carbonyls $M_x(CO)_y$ generated by the codeposition of alkali metals and CO in an inert gas matrix at 10 K. C.N. Krishnan, R.H. Hague and J.L. Margrave, J. Mol. Struct. 157 (1987) 187.

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