129Xe NMR Study of the Homogeneity and the Size Distribution of Small Sodium Metal Particles in NaY Zeolite

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Received September 21, 1994; revised December 20, 1994

Abstract. NaY zeolite samples loaded with sodium metal by vapor phase deposition have been investigated using 129Xe NMR spectroscopy. At low sodium concentration, the 129Xe NMR spectrum showed three resonance lines which clearly indicate the existence of distinct domains in the zeolite sample. Such an observation suggests that the diffusion of the xenon atoms into each domain only occurs with respect to the NMR time scale (2.9 ms). As the sodium concentration increases, observation of a single broad line indicate a macroscopic homogenization of the system. The shift of this line is explained in part due to a paramagnetic interaction between the xenon atoms and the unpaired electrons of particles containing an odd number of sodium atoms. The linewidth is due to the distribution of the local magnetic fields partially averaged by the rapid motion of the xenon atoms and to the statistical distribution of the sodium particles in the supercage cavities. The paramagnetic interaction vanishes with the oxidation of the sample leading to a narrowing and a shift of the line to higher magnetic fields.

1. Introduction

The 129Xe NMR of adsorbed xenon atoms is very sensitive to the zeolite environment and serves, therefore, as a useful probe for studying the adsorption and the distribution in the zeolite supercage cavities of organic molecules or transition metal particles [1-18]. It is well known, since the pioneering work of Rabo et al. [19], that zeolites are also an interesting matrix for producing and studying small sodium metal particles. They have shown that two distinct species are formed in a NaY zeolite loaded with sodium metal [19]. At low sodium concentration, Na43+ clusters are formed in the sodalite cage. Using ESR techniques, these clusters are detected by a hyperfine structure of 13 lines [20–22]. As the sodium concentration increases, a narrow line appears and grows at the center
of the hyperfine structure. This line is attributed to an excess of sodium atoms which form small particles in the supercage cavities of the NaY zeolite. A Curie-type spin susceptibility and a temperature independent EPR linewidth clearly show evidence for quantum size effects in these particles [20–24]. Following recent work [25] we have extended our $^{129}$Xe NMR study to zeolite samples with different sodium concentrations. As we have mentioned above, this technique provides an opportunity to obtain important information on the macroscopic homogeneity and the size distribution of the sodium particles.

2. Experimental Section

NaY zeolite has been synthesized at the School of Chemistry in Montpellier using a standard procedure [26]. Scanning electron microscopy experiments established NaY crystallite grain diameters of about 1 μm. The zeolite was dehydrated in a gradient furnace at 750 K under vacuum (10$^{-5}$ torr) overnight. The temperature was then lowered to 520 K and the zeolite was exposed to sodium vapor. After the reaction, the temperature was slowly cooled down to room temperature to avoid a severe thermal gradient. Among the prepared samples three samples were prepared for this study, referred to as Na-NaY1, Na-NaY2 and Na-NaY3 systems, with increasing sodium exposure times (1, 2 and 8 h, respectively). As the sodium concentration increases, the color of the samples turns from bright red to black. Chemical compositions were calculated from the elemental analysis after dissolution, performed by the SCA CNRS in Solaize (France). This chemical analysis has shown that the average number of sodium metal atoms in the zeolite supercage cavities is 1.0±0.1, 2.0±0.1 and 8.0±0.1 for the Na-NaY1, Na-NaY2 and Na-NaY3 samples, respectively. For the Na-NaY1 and Na-NaY2 samples, the chemical analysis was done after an annealing where a part of the sodium atoms has diffused out of the zeolite sample. Using break-seal containers, these samples were transferred under vacuum to a 10 mm NMR tube equipped with a glass vessel stopcock and exposed to a given equilibrium xenon pressure. An unloaded sodium NaY zeolite was also dehydrated overnight under vacuum at 750 K and used as a reference for this study. $^{129}$Xe NMR spectra were obtained at room temperature with an AC250L Bruker spectrometer operating at a frequency of 69.19 MHz. Xenon gas (Air Liquide, 99.995 %) was used in this study. Typically, 2000 signal acquisitions were accumulated for each spectrum with a recycle delay of 0.5 s between $\pi$/2 pulses. Chemical shift measurements are precise to within 1 ppm and are expressed relative to xenon gas at zero pressure [27]. Downfield (high frequency) chemical shifts are considered to be positive. Our samples are air sensitive and immediately decolors when they are exposed to the air. Also we do not know the exact weight of the samples. Because of that we are not able to measure the xenon isotherm and we can only present our results as a function of xenon pressure.