A VIBRATIONAL STUDY OF TETRACYANOETHYLENE ADSORBED ON MAGNESIA.

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ABSTRACT. The saturation adsorption of tetracyanoethylene (TCNE) from the vapor phase onto magnesia activated at 200 and 400 C is studied. Fourier transform infrared and electron spin resonance spectroscopy are used to characterize the chemisorbed material. FT-IR spectra of authentic samples of TCNE, TCNE-l, TCNE-2, and the tricyanovinylalcoholate anion (TVA) are also reported for comparison purposes. We find that the uptake of TCNE as a function of activation temperature is most closely related to the surface hydroxyl coverage. It does not correlate well with the BET surface area. We also find that the primary chemisorption product is a TVA like species (perhaps polymeric). Radical signals are detected, presumably from TCNE-l, but correspond to less than 5% of the chemisorbed TCNE.

1. Introduction

There is a continuing interest in the redox chemistry of TCNE with various surfaces1-25. The early work was directed toward the detection and identification of radicals formed by chemisorption on oxides1-12. Only recently has surface vibrational spectroscopy been applied extensively to this area of research13-25. In the case of TCNE adsorption on alumina, it was shown that the radical anion of TCNE, TCNE-l, was not the major chemisorption product13-17. The non-radical dianion, TCNE-2, and the tricyanovinylalcoholate anion, TVA-l, are also formed in significant quantities.

FT-IR, Raman, and EELS studies of TCNE adsorbed on single crystal metals and on electrode surfaces have yielded results that are surface dependent18-25. On carbon electrodes both the dianion and TVA-l are observed20. In contrast, the radical anion is the principal species reported on platinum electrodes21-23. Both the dianion and the radical anion are reported to be formed on Cu(lll)18,19, but only the radical is reported on Ni25.

The surface dependence of the mechanism and extent of chemisorption of TCNE on various surfaces is interesting but not well understood. The present paper is the first of a series in which we probe the redox adsorption of TCNE.
Here we will focus on the adsorption of TCNE from the vapor on magnesia activated at 200 and 400 °C. Below ca. 300 °C the sample is formally magnesium hydroxide. Above ca. 360 °C it is properly thought of as MgO with bound hydroxyl groups. During the decomposition of Mg(OH)\(_2\) the surface area of the sample rises markedly. Thus, adsorption at these two temperatures should provide insight into the role of hydroxylation and surface area on the chemisorption of TCNE.

2. Experimental

2.1 MATERIALS: TCNE was purchased from Aldrich Chemical Company and purified by sublimation through Alpha Products 28 mesh activated charcoal at 100 °C. The Mg(OH)\(_2\) was used as purchased from Alpha Products. Authentic samples of KTCNE, CsTV A, and Na\(_2\)TCNE were prepared by previously described methods\(^{13-16}\).

2.2 SAMPLE PREPARATION AND HANDLING: Oxide activation and TCNE chemisorption were carried out under vacuum on a standard grease-free double (UHP N\(_2\) / LN\(_2\)-trapped vacuum) manifold in a demountable 2-chamber cell. Each chamber of the glass cell was isolated by a greaseless Teflon valve. First the TCNE (ca. 0.1g) was loaded and pump-purged and then sealed under vacuum. The amount of TCNE always exceeded the maximum possible uptake by the magnesia sample. Then, the Mg(OH)\(_2\) (ca. 1.0g) was loaded in the second chamber and the adsorption cell was again attached to the manifold. Typically, 4 activations were carried out simultaneously by heating 4 samples to the desired temperatures for >12 hrs under vacuum (<10\(^{-5}\) torr). A TCNE free activated sample (blank or reference magnesia) was always prepared with the TCNE adsorbed sample. Following activation, the vacuum valve was closed and the oxide was cooled to 100 °C and the TCNE chamber was heated to the same temperature. The valve separating the chambers was then opened. Both chambers and valves were maintained at 100 °C for 4 hours. At the end of this period, the TCNE sidearm was cooled to LN\(_2\) to remove the residual TCNE vapor from the chamber containing magnesia. After condensation of the TCNE the TCNE chamber was closed and the entire cell was brought to room temperature. At this point 1 atmosphere of nitrogen was introduced into both chambers. Each chamber was closed and the cell was transported to a Vacuum Atmospheres inert atmosphere glove-box. Post adsorption handling occurred within the glove-box.

The amount of residual TCNE was collected and weighed to determine (by difference) the total TCNE chemisorption. Because condensation of TCNE occurred over most of the surface of the chamber and on the valve stem, the possible error in this number was large, of the order of 50%.