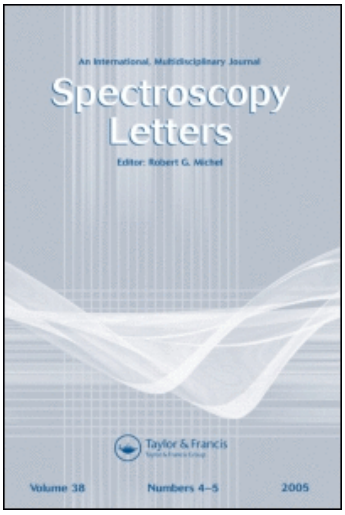

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SERS and IR Studies of the Reaction of an Oxidized Surface and an Etched Surface of Copper with 2-Mercaptobenzimidazole

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SERS AND IR STUDIES OF THE REACTION OF AN OXIDIZED SURFACE AND AN ETCHED SURFACE OF COPPER WITH 2-MERCAPTOBENZIMIDAZOLE

Keywords: Surface enhanced Raman scattering, reaction, surface, copper, oxide, 2-mercaptobenzimidazole

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Abstract

Chemisorption of 2-mercaptobenzimidazole (MBIH) on copper surface has been investigated under different conditions by the use of surface enhanced Raman scattering (SERS). We found that MBIH could chemically reacted with an acid cleaned surface in the presence of air at room temperature, and that it reacted with an oxidized surface only at elevated temperature under the experimental conditions. The reaction product was copper 2-mercaptobenzimidazolate.

Introduction

Azoles such as 2-mercaptobenzimidazole (MBIH) have found widespread use as corrosion inhibitors for copper and its alloys. MBIH is also of great interest as a lingand. In a neutral solution, MBIH coordinates with a metal ion via the sulfur lone pair electrons. Adsorption of this inhibitor onto copper from aqueous solution results in formation of surface films.[1-2] It appears that this surface film can act as a barrier to cathodic reactions, thus imparting some degree of corrosion resistance to the copper substrate. In recent years there have been considerable efforts devoted to the characterization of the surface films formed during the exposure of copper to corrosion-inhibitive solutions and various possible structure have been proposed. The mechanisms leading to the film formation, however, still remain uncertain.[3] The consensus is that azole is chemisorbed on the copper oxide surface to form a polymeric complex film.[4] Most of the reports in the literature concerning Cu-Azole complex formation are related to the reaction of azole with copper cations or copper oxides. Rhodin and Tompkins found that exposure of freshly cleaned copper in air would produce Cu_2O film. XPS and quartz microbalance measurement indicated the thickness of the Cu_2O film reached a constant value, about 10-15 angstroms, after

1 h.[5] Tompkins also found that dipping a copper foil into 2-methylbenzimidazole solution for 1 min at room temperature could produce a complex film of hundreds of angstroms thick.[6] Since the copper foil was only covered with 10 angstroms of Cu_2O before immersion, as reported in his paper,[6] we believe that azoles might react with Cu at zero oxidation state as well as with copper oxides.

The past decade witnessed a dramatic growth in the use of surface enhanced Raman scattering (SERS) technique to elucidate the chemical structures and bonding of molecules adsorbed on metal surfaces.[7-9] We have taken advantage of the high sensitivity of SERS (enhancement factors up to 10^6) to study the molecular structure of MBIH species on copper surfaces, resulting in the discovery of a chemisorbed complex film of cuprous 2-mercaptobenzimidazolate (Cu^+MBI^-) on metallic copper. In this work we will compare the reaction rate of MBIH on a freshly etched surface with that on an oxidized surface of copper. We find that SERS, if combined with other techniques, is an excellent spectroscopic tool for the study of thin films since it is very sensitive to the first couple of monolayers.

Experimental Section

MBIH was purchased from SHanghai Chemical Co. and was purified by recrystallization from ethanol before

use and dissolved in ethanol to make solution with concentration of 0.001 M. As a sampling substrate for SERS studies, a copper foil was immersed in 2 M HNO_3 solution. After about 10 seconds, a number of bubbles formed near the surface. Vigorous agitation had been applied for 3-4 min before the roughened copper foil was rinsed with distilled water and dried by blowing with nitrogen gas. The detailed procedure has been reported elsewhere.[10] The etched copper foil was immersed into MBIH solution with pH 4 for 2 min. The surface-adsorbed moieties were characterized by SERS and XPS. In a bulky reaction study, 0.5 g of HNO_3-etched copper powder was mixed with 100 mL of 0.01 M MBIH solution and stirred for 2 days. After reaction, all of the copper powder was turned into a yellow solid material which was supposed to be the powdered reaction product and was characterized by IR and element analysis.

The SERS spectra were measured with a backscattering geometry in air on a SPEX-1403 Raman spectrometer. The incident laser excitation was 647.1 nm from a Kr^+ laser source with out put power of 20-100 mW. IR spectra were recorded with a Nicolet 170 SX FT-IR spectrometer. X-ray induced Auger spectroscopy (XAES) were obtained by means of an ESCA LAB MK-2 spectrometer with Mg-$K\alpha_{1,2}$ as the exciting source (hv=1253.6 eV).

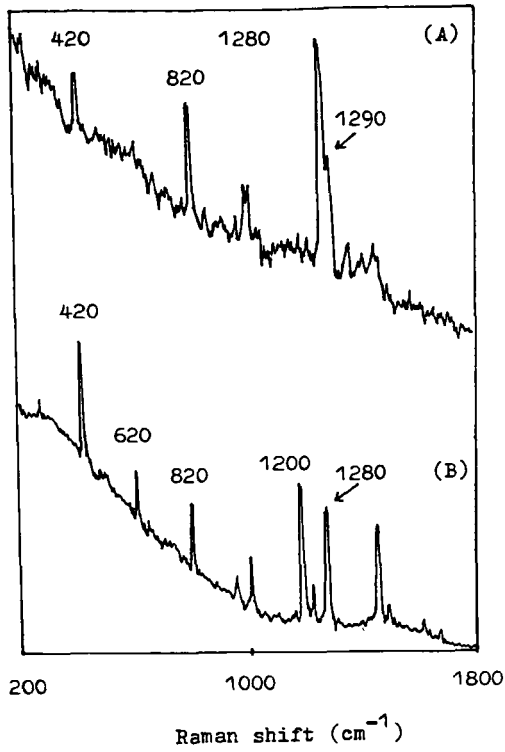


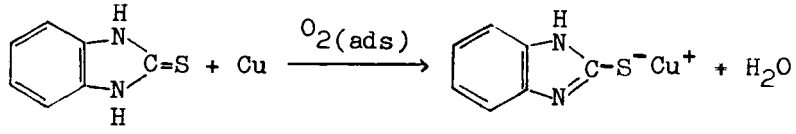
Figure 1. SERS spectrum of MBIH on metallic surface of Cu (A) and normal Raman spectrum of neat MBIH (B).

Result and Discussion

Figure 1 shows a normal Raman spectrum of MBIH and a SERS spectrum of MBIH adsorbed on copper foil which had been immersed in a solution with pH 3-4 at 20 °C.

The normal Raman spectrum (Figure 1B) shows benzene ring vibration modes near 1280, 1025, and 420 cm^{-1} [11], C=S bending vibration lines at 620 cm^{-1} and 1232 cm^{-1},[12] and SCN-H bending mode at 1200 cm^{-1}.[12]

In Figure 1A, however, the C=S vibration bands disappeared, and the SCN-H band was not only shifted from 1200 to 1290 cm^{-1} but also reduced one half in relative intensity. The reason of frequency shift for 1200 cm^{-1} line is probably due to the ionic effect resulted from the interaction between MBIH and Cu in the presence of air. Since the solution was slightly acidic (pH = 3-4), there was no oxides on Cu surface. We propose that during the immersion treatment, MBIH adsorbed onto the metallic surface and then chemically reacted with co-adsorbed oxygen which comes either from air or from solution.



MBIH $Cu^{+}MBI^{-}$

There was a consensus that azole could react with copper only when it is covered with oxides.[12] However, our SERS study clearly indicated that MBIH could reacted with metallic copper in a faster rate than with copper oxides. Figure 2 illustrates SERS spectra of MBIH on a preoxidized surface of copper.

As the copper foil was exposed to air for 2 h after etching, a Cu_2O film of 12 angstroms thickness formed

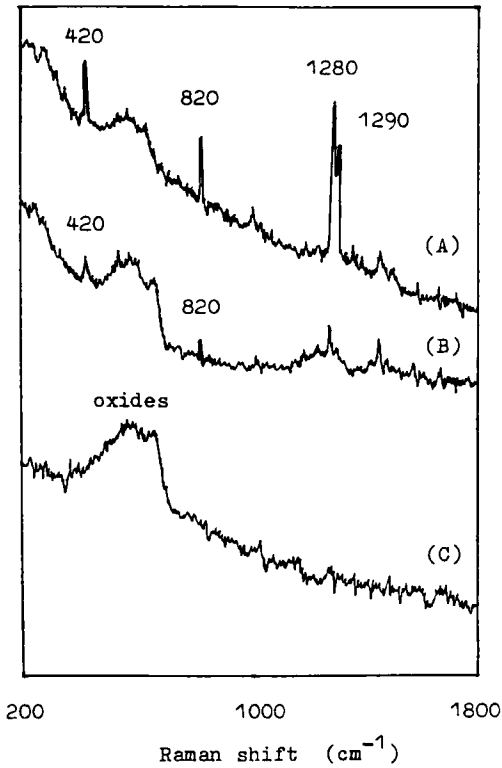


Figure 2. SERS spectra: (A) Cu foil exposed to air for 2 h; (B) after immersion at room temperature; (B) after immersion at 60 °C.

on the surface.[6] Figure 2A shows the bands of oxides in the 510-590 cm^{-1} region explicitly. When the preoxidized foil was immersed in a neutral MBIH solution (pH = 6.5) for 2 min at 20 °C, we found that the Raman signal intensities of the adsorbed MBIH (Figure 2B) were rather weak, as compared with those

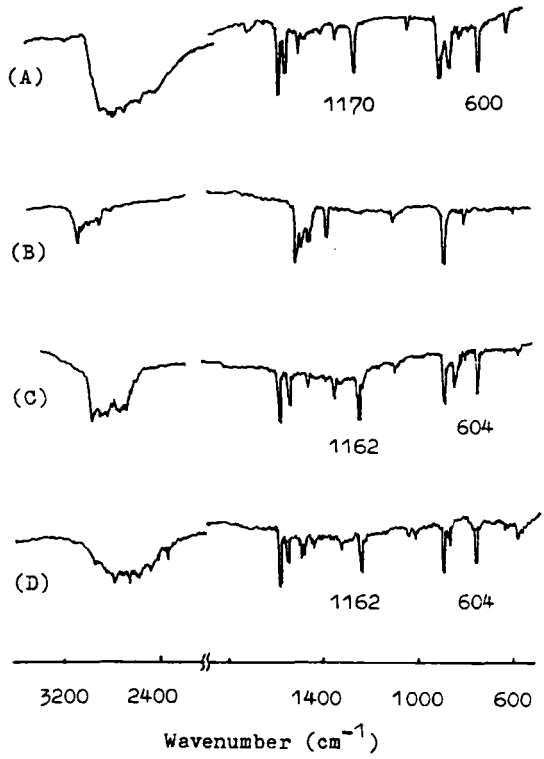


Figure 3. IR spectra: (A) neat MBIH; (B) reaction product of MBIH with Cu powder; (C) reaction product with Cu_2O; (D) reaction product with CuO.

in Figure 1A. Therefore the cleaned surface of copper could adsorb MBIH anchored directly to the metal while the oxidized surface did not reduce the amount of oxides significantly after immersion at 20 °C. Immersion the preoxidized Cu into a warm solution (60 °C) could provide a better SERS spectrum as illustrated

in Figure 2C. Figure 2C shows appearance of Raman lines of chemisorbed MBIH and reducing the amount of oxide bands indicating that MBIH reacted with the oxidized surface in a warm solution. By the comparison of Figures 1 and 2, we found that MBIH could react with a metallic surface at room temperature while it reacted with an oxidized surface at elevated temperature.

It is necessary to get further evidence for the surface reaction. Infrared (IR) spectroscopy analysis, complementary to SERS measurement, was carried out. Figure 3 shows IR spectra of the reaction products separated from the mixture of MBIH solution of pH = 3-4 with Cu, Cu_2O, and CuO respectively.

IR spectrum of MBIH in solid state (Figure 3A) shows strong and broad bands in region 3300-2500 cm^{-1}, which are due to the hydrogen bonded N-H stretching. In figure 3B recorded from the reaction product, the decrease in intensity of the N-H stretching bands and the disappearance of C=S bands at 600 and 1170 cm^{-1} confirmed the deprotonation of N-H group and the opening of C=S bond. The purpose of using a pH 3-4 solution of MBIH in this study is to avoid the confusing of surface oxides on copper, because they are not supposed to exist in the form of Cu_2O or CuO on the surface in an acidic medium. XAES study indicated the presence of Cu^+ in the product. Elemental analysis provided its stoichiometry of Cu^+MBI^-.

Spectra 2C and 2D were recorded from the reaction products of cuprous and cupric oxides in MBIH solution, which show the remaining SCN-H bending mode at 1162 cm^{-1} and C=S bending mode at 604 cm^{-1}, indicating that MBIH did not deprotonate during the reactions with copper oxides. The spectral difference are obvious between Figure 3B and the others. IR, XAES, and elementary analysis data strongly supports the conclusion from SERS measurements.

Conclusion

We have shown that, in the presence of air, 2-mercaptobenzimidazole can react with a chemically cleaned surface of copper other than copper cations or copper oxides under extremely mild conditions. The reaction rate of MBIH with copper metal and oxygen is much faster than that with copper oxides.

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