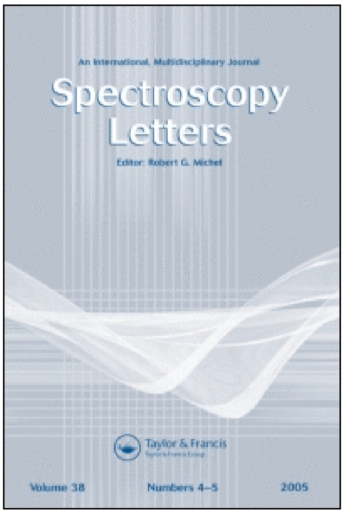

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FTIR-RAS Studies of the Coordination of Surface Oxide Layers of Copper with Poly(acrylonitrile)

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FTIR-RAS STUDIES OF THE COORDINATION OF SURFACE OXIDE LAYERS OF COPPER WITH POLY(ACRYLONITRILE)

Keywords: Infrared reflection-absorption spectroscopy, Pan, Metal, Surface, Coordination.

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ABSTRACT

The effect of surface oxide layers on the coordination of polyacrylonitrile (PAN) to copper has been investigated by infrared reflection-absorption spectroscopy. It has been found that side-on coordination can be formed for PAN on copper surface preoxidized at 200 °C for 30 min. On the other hand, no coordination is observed for PAN adsorbed on freshly cleaned copper which had been heated at 200 °C for 90 min in vacuum. However, the side-on coordination is also found on the freshly cleaned copper after an additional heating at 180 °C for 90 min in air. We proposed that these results are likely due to the variation in chemical reactivity of copper in different oxidation states. It has also been found that the side-on coordination of copper to $C\equiv N$ groups can facilitates the cyclization of PAN at lower temperatures.

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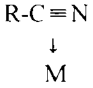
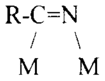
INTRODUCTION

From the studies of the metal-nitrile complexes and nitriles adsorbed on metal surfaces, it is well known that the $C\equiv N$ functional group can be bonded to a metal center in three different types of coordination [1-6]: (1) σ-bonding (the end-on coordination) through the lone pair electrons on the N atom, which generally results in an increase in the $C\equiv N$ stretching frequency from that of the free molecules in the IR spectra[2,3]. (2) π-bonding (the side-on coordination) through the triple bond, which generally results in a decrease in the $C\equiv N$ stretching frequency [4,5]. (3) di-σ bonding through the C and N atoms of the $C\equiv N$ group, which substantially reduces nitrile group bond strength. As a consequence, the CN stretching frequency occurs at about 1600 cm^{-1}, a frequency in region characteristic of the C=N double bond [1].

$R\text{-}C\equiv N: \rightarrow M$ (σ-bonding) (I)



$R\text{-}C\equiv N \downarrow M$ (π-bonding) (II)



$R\text{-}C{=}N$ with M M (di-σ bonding) (III)

Polyacrylonitrile (PAN) is a commercially important and widely used polymer [7]. PAN has a strongly polar nitrile group attached to alternating carbons on a saturated hydrocarbon. It has been established that PAN undergoes polymerization of the nitrile groups followed by conjugation of the hydrocarbon backbone upon pyrolysis [8-10]. Although the pyrolysis chemistry of PAN has been extensively investigated, far fewer studies of PAN with metal ions, especially that on metal surfaces, have been published [11-15].

Wu and Liedberg [13] have found the chemical structure of thin films of pyrolyzed PAN on copper is quiet different from that on aluminum because Cu(I)-nitrile complexing occurs. Conclusive evidence was found for end-on coordination to copper through nitrogen lone-pair orbitals of the $C \equiv N$ groups. Preliminary results indicated also the presence of side-on coordinated nitriles in PAN. In additional, they found a tendency for the end-on form to increase in number with heating time at the expense of the side-on form.

The previous work in our laboratory has showed the metallic copper can catalyze the gelation of PAN solution in dimethylformamide. The copper exists in the gel as the Cu^{++} ion as in the reacted copper sheet surface [12]. Our surface-enhanced Raman scattering (SERS) studies of PAN on Ag foil provided information concerning adsorption-induced cyclizaton under room temperature [14,15].

In this paper, we describe the results of our recent studies about the effect of the surface oxide layers on the coordination of PAN and the pyrolysis chemistry of PAN on the metal surface. Our interest in this system derives from the conjecture that different copper oxidation states will exhibit different abilities to coordinate with PAN. The detailed scrutiny of PAN/metal surface systems would provide further insight into the reactivity in surface chemistry.

EXPERIMENTAL

All regents were commercially available from Shanghai Chemical Co. and were of chemically pure grade.

After removal of the polymerization inhibitor by distillation under reduced pressure, acrylonitrile initiated by potassium persulphate were polymerized in a water slurry at 50 °C [16]. The polymer was carefully washed with methanol and dried in vacuum at 60 °C overnight.

The chemically cleaned copper sheets were first polished as mirror and etched with dilute HNO_3 for 3 s, then rinsed with water and ethanol for several times. These freshly cleaned copper plates were either quickly immersed in a very dilute PAN solution (10^{-5} M) in N,N-dimethylformamide (DMF) or preoxidized at 200 °C for 30 min in a mechanical convection oven and then immersed in PAN solution. The samples were dried in vacuum for 48 h to evaporate the solvent. Pyrolysis of PAN on copper surface was carried out in vacuum.

The infrared spectra were recorded in the frequency range 4000-500 cm^{-1} with a BRUKER RFS 66V Fourier-transform spectrometer fitted with a reflection-absorption accessory and a KRS 5 wire grid polarizer. The spectra were obtained with the IR beam polarized with its electric field vector parallel to the plane of incidence and at an angle of incidence of 88°.

RESULTS AND DISCUSSION

The reflection-absorption spectra of PAN in bulk, on freshly cleaned copper and on preoxidized copper are shown in Fig. 1 A, B and C, respectively. The band at 1454 cm^{-1} corresponds to CH_2 bending mode. The bands around 2244 cm^{-1} are assigned to $C\equiv N$ stretching vibration. The observation of the same position and bandwidth of this band in Fig. 1B and Fig.1C indicates the existence of the freely dangling (uncomplexed) $C\equiv N$ groups in PAN layers. A weak and broad band centered at 2189 cm^{-1} in Fig. 1C also attributed to the $C\equiv N$ stretching mode [4,5,16]. The substantial red shift (about 55 cm^{-1}) and band broadening upon adsorption indicate the direct interaction (side-on coordination) between the cyano groups and the preoxidized copper surface. Here, the presence of side-on coordination of $C\equiv N$ groups of PAN on copper corroborates Chun's proposal that this fashion is favored

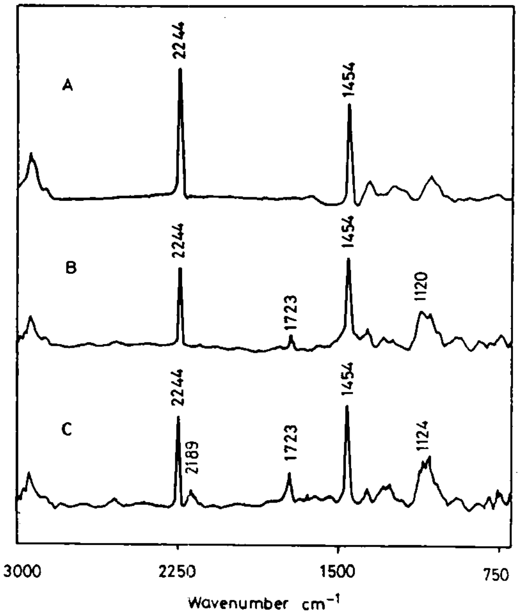


Fig. 1 Reflection-absorption infrared spectra of PAN: (A) in bulk, (B) on freshly clean copper, (C) on preoxidized copper.

when the CN group is not conjugated with the neighboring unsaturated group [17]. A similar phenomena has been observed in the case of aliphatic dinitriles adsorbed on copper surfaces in SERS studies [18]. It is also consistent with our previous studies about chemisorption and reaction of PAN on Ag [14,15,19]. Therefore, the 2189 cm^{-1} band implies that the coordination of preoxidized copper surface to the cyano groups brings about back donation of electrons from the metal to the C$\equiv$N antibonding orbitals, reducing the C$\equiv$N triple bond order [13,19].

The observed difference in spectrum between Fig. 1B and Fig. 1C is likely due to the variation in chemical reactivity between PAN and the surface oxide layers. Rhodin and Tompkins found that exposure of freshly cleaned copper in air would produce Cu_2O film and the thickness of the Cu_2O film was 10-15 Å[20,21]. SERS studies on the air oxidation of copper also showed the oxide bands for 30 min exposure at room temperature correspond to 2-3 monolayers of Cu_2O [22]. On the other hand, a thin CuO film (less than 5.0 nm) was formed on the copper surface by heating at 200 °C for 30 min and below the CuO film was a thicker Cu_2O film (20-25 nm). The thickness of both CuO and Cu_2O films was increased by heating at higher temperature and longer time [23]. Therefore, it is reasonable to assume that the reactivity of CuO on the preoxized copper surface is higher than that of Cu_2O on the freshly cleaned copper surface.

It is interesting to note the bands around 1723 and 1120 cm^{-1} in Fig. 1, they correspond to the C=O and C-O stretching vibration modes, respectively [22]. We believe that some nitrile groups are converted to carboxyl groups and copper has a catalytic effect on the hydration of nitriles [12].

The reflection-absorption infrared spectra of PAN on preoxidized copper and freshly cleaned copper after heating at 200 °C for 90 min in vacuum are shown as spectra A and B in Fig. 2, respectively. New appearance of bands around 1590 cm^{-1} are assigned to C=C or C=N conjugation ring stretching vibrations, indicating that PAN has partially undergone structural changes in this case. The observation is consistent with previous studies reported by Wu et al [13]. Copper surface appears to have a catalytic effect on the rate of cyclization or backbone conjugation.

The band at 2243 cm^{-1} in Fig. 2B, having the same position as that in Fig. 1B, implies that $C\equiv N$ group is still freely dangling, no coordination of copper to the cyano groups is observed on the freshly clean copper surface heated in vacuum. However, after additional heating at 180 °C for 90 min in air, non-preoxidized copper surface shows a different spectrum. The $C\equiv N$ mode of the free ligand is no longer present (Fig. 2C). Instead, a broader band appears at 2190 cm^{-1}, implying side-

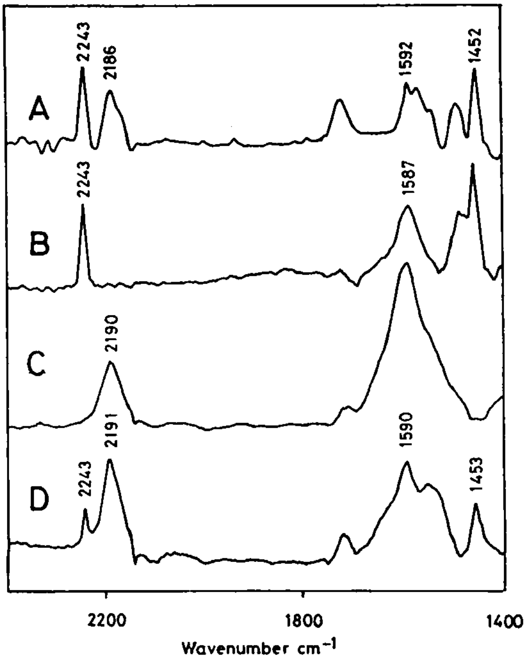


Fig. 2 Reflection-absorption infrared spectra of PAN on : (A) preoxidized copper after heating at 200 °C for 30 min in vacuum, (B) non-preoxidized copper after heating at 200 °C for 30 min in vacuum, (C) non-preoxidized copper after heating at 200 °C for 30 min in vacuum and additional heating at 180 °C for 90 min in air, (D) non-preoxidized copper after a separate heating at 180 °C for 90 min in air.

on coordination of C≡N groups is observed on the prepared copper surface. We attribute this change in spectra to the fact that the freshly cleaned copper surface adsorbed oxygen during heating in air [22], and a thin CuO film was formed above Cu_2O layer. In addition, as can be seen in Fig. 2C, CH_2 bending modes at 1452 cm^{-1} disappears nearly and the band around 1587 cm^{-1} becomes strong. Thus, it is seemly that nitrile complexing and cyclization occur at the same time.

Fig. 2D shows the reflection-adsorption infrared spectrum of PAN on the freshly cleaned copper surface after heating at 180 °C for 90 min in air. Similarly, the major bands at 2243, 2191, 1589, 1453 cm^{-1} are observed. Therefore, with the incorporation of oxygen, PAN molecules has undergone nitrile complexing as well as partial cyclization and conjugation reaction on copper surface exposured to hot air. The result confirms our above conjecture that a higher reactivity of CuO rather than Cu_2O toward PAN.

Fig. 3 shows the transmission infrared spectrum of PAN film containing Cu^{++} ions (10 mmol Cu^{++} in 1 g PAN) in the 2400-2100 cm^{-1} region. The same observations of $C\equiv N$ band at 2240, 2192 cm^{-1} indicates the Cu^{++} ions coordinate the cyano groups through the triple bond. Thus, we propose that copper exists in complex as Cu(II) form as in the reacted copper oxide surface.

It is well known that, at a relatively high temperature (300-400 °C), PAN can undergo cyclization through the cyano groups along the chains, yielding a double-coupled conjugated ladder polymer [8,24]. Copper surface appears to have a catalytic effect on the rate of cyclization or backbone conjugation, for bands around 1589 cm^{-1} which are assigned to C=C or C=N stretching vibration modes are observed in spectra of PAN on copper after heating at 200 °C for only 90 min. Since the nitrile complexing and cyclization reactions are observed at the same time, it is reasonable to assume that the side-on coordination of copper to the cyano groups of PAN, which weaken the $C\equiv N$ triple bond, can facilitate the cyclization of PAN on copper at temperatures 100-200 lower than for bulk PAN. Based on above results, we propose the pyrolysis chemistry of PAN on copper is different from that in bulk.

A further detail studies have been carrying out to clarify the effect of copper surface on the rate of cyclization and complexing reactions. The results will be addressed in a subsequent paper.

CONCLUSION

We have demonstrated that copper oxide has a significant effect on the formation of copper-nitrile complexing by using FTIR-RAS. The reactivity of thin CuO film is

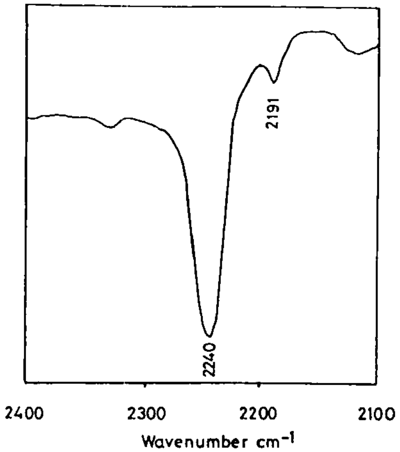


Fig. 3 Transmission infrared spectrum of PAN film containing Cu^{++} ions.

proposed to be higher than that of Cu_2O film toward PAN. The side-on coordination of PAN to copper through triple bond of the $C \equiv N$ group is found and it is likely that oxygen is important for this bonding. The results also indicate that copper exists in Cu(II) state in PAN after complexing. In addition, the cyclization and conjugation reactions occur at the same time as complexing, thus implying the pyrolysis chemistry of PAN on copper is different from that in bulk.

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