

A STUDY OF THE MECHANISM OF ADSORPTION OF ETHYL CELLULOSE ON SILVER POWDER

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Abstract

The mechanism of adsorption and desorption of ethyl cellulose (EC) on and from silver powder was studied. After analysis with DSC, XPS and dynamic FT-IR, which could be heated by a program-controlled heater, applied to observe the states of pure EC and of EC adsorbed on silver powder, and also the thermal decomposition of EC from silver powder, the chemisorption bonding bridge between the oxygen atoms of EC and the silver atoms investigated. The differences in thermal decomposition between pure EC and EC adsorbed in silver powder were also studied. It was concluded that the chemisorption bonding between the oxygen atoms of EC and the silver atoms mainly involved the lone-pair electrons of the oxygen atoms on the EC chain and the outer empty $5sp^3$ hybrid orbital of the silver. Because of the formation of this bridge, the bonds between neighboring carbon and oxygen atoms are weakened. As a result of this effect, the C-O bonds in the EC chain are broken more easily than the C-H bonds, which leads to the observation of -C-H- fragments in the upper space when EC adsorbed on silver is heated. When the same experiments were carried out on pure EC, almost all kinds of broken fragments of the EC molecule, including -C-H-, -C=O- and -C-O- appeared simultaneously.

Keywords: chemisorption, desorption, DSC, dynamic FT-IR silver powder, XPS

Introduction

In earlier work [1, 2], the character of the adsorption of ethyl cellulose on silver powder in ethyl acetate solution was studied. We have introduced various parameters and the relative calibrated quantity of the surface fractal for silver powder to characterize the silver powders obtained under different technological conditions. In order to establish the adsorption mechanism and to understand the desorption, the thermal decomposition and the oxidation, it is necessary to analyse the formation of bonds between various atoms and the breakdown of bonds.

Ethyl cellulose is a polymer with the unit structure shown in Fig. 1. The oxygen atoms are seen to be in a unique chemical environment, i.e. there are two lone-pair electrons in the oxygen sp^3 hybrid orbital. When the $5sp^3$ hybrid orbit of silver approaches these oxygen atoms, there will be a strong bonding tendency between them. The distortion of the electron cloud will result in a chemical shift in the XPS spectrum. Thus, we can obtain information on the bonding of silver and oxygen by XPS analysis.

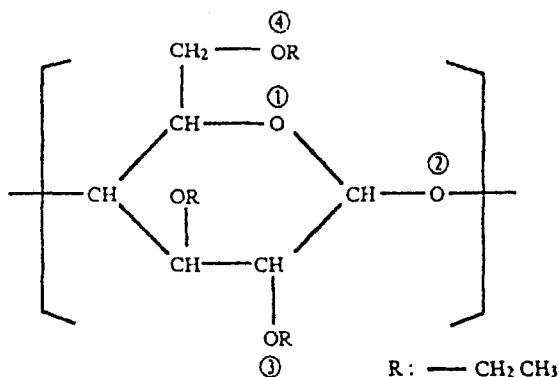


Fig. 1 The structural unit of ethyl cellulose

Quantum chemical calculations on the adsorption of ethylene oxide (C_2H_4O) or ions on Ag(110) [5, 6] show that the contribution of Ag orbits to the adsorption bond is as follows: $5s=25\%$, $5p=71\%$ and $4d=4\%$. The charge is transferred mainly from the lone-pair electrons to the silver atom; the transfer of charge from silver toward the empty orbitals of the adsorbate is negligible.

In this paper, XPS is used to investigate the chemisorption bonding, while DSC is used to determine the kinetic parameters of decomposition-oxidation of ethyl cellulose under different conditions. In order to obtain detailed information on the desorption and decomposition process, dynamic FT-IR involving the application of a program-controlled heater is also used.

Experimental

Sample preparation and pretreatment

Superfine silver powders were prepared by reduction of Ag_2CO_3 , while 'shining silver powder' was further processed by a mechanical method. Although the silver powders were washed in the preparation, they were washed again in ethylene glycol with a supersonic stirrer. The samples were then immersed in ethyl acetate solution containing 2.1 g l^{-1} ethyl cellulose to implement adsorption treatment. The treatment was initially accompanied by supersonic stirring. Afterwards, the whole system was set aside for 24 h. The completely adsorbed silver powder was then separated by a high-speed centrifuge. The treated silver powder was washed three times with analytical grade acetone to remove surplus adsorbate not really chemically adsorbed. The silver powder was separated from the washing reagent and dried thoroughly in a desiccator at room temperature to be ready for testing.

In order to keep the same experimental conditions, the activation energy of decomposition of pure EC was measured by DSC by using an EC film on the wall of an aluminium crucible; this was obtained from ethyl acetate solution in the same way as above after the ethyl acetate was evaporated off. It is necessary that the EC film and the EC adsorbed by the silver powder should have almost the same quantity.

X-ray photoelectron spectroscopy (XPS) analysis

XPS was carried out on a PHI5500 ESCA instrument. A Mg anode ($h\nu=1253.6$ eV) was used and the pass energy was 58.7 eV. The energy scale was calibrated by means of $\text{Cu}3p^{3/2}$ (75.1 eV), L_3MM (334.9 eV) and $2p^{3/2}$ (932.7 eV). The base vacuum was better than 5×10^{-8} Pascals. The sample charge was eliminated by positioning the binding energy of Cls for C-H and C-C bonds at 284.8 eV. The asymmetry function was applied to the curve fit of O1s.

Differential scanning calorimeter analysis

A thermoflex DSC was used for DSC analysis. The scanning speeds were 2.5, 5, 10 and 20 K min^{-1} . The full scale for thermal flow was ± 5 – ± 10 mW and the chart speed was 5–40 mm min^{-1} . The experiment was carried out in a static air atmosphere. The reference material was α -alumina powder and an aluminum crucible was used. The quantity of silver powder in the ethyl cellulose adsorption test was about 20 mg. The decomposition and oxidation activation energy was calculated by the Kissinger [8] method.

Dynamic FT-IR analysis

The dynamic FT-IR analyses were carried out on a NICOLET 170SX spectrometer. For detection of the decomposition fragments of EC easily and effectively, we devised a 50 mm long 'heating decomposition cavity with semi-sealing' (Fig. 2) and treated it as a gas cell. The sample could be heated by a program-controlled heater and the experiments were carried out between 400 and 4000 cm^{-1} by using the adsorption spectrum method with a resolution of 4 cm^{-1} . The baseline was automatically corrected in calculations of adsorption peak areas.

Results and discussion

XPS results

The results of XPS analysis on superfine silver powder, shining silver powder and pure EC are shown in Table 1 and Fig. 3. Only the O1s spectrum changed greatly. The O1s spectrum of pure EC exhibited only one peak, at 532.5 eV, while the two silver powders gave two peaks. The 532.9 eV peak should correspond to the oxygen in ethyl cellulose and the 530.6–530.7 eV peak to the oxygen atom on silver

Table 1 Binding energy of corresponding electron obtained from XPS (eV)

Sample	O1s			Cls	Ag3d	
	before ads.	after ads.				
Pure EC		532.5		284.8	286.3	
Superfine Ag	530.7	530.7	532.9	284.8	286.4	368.2
Shining Ag	530.8	530.7	533.0	284.8	286.4	368.2

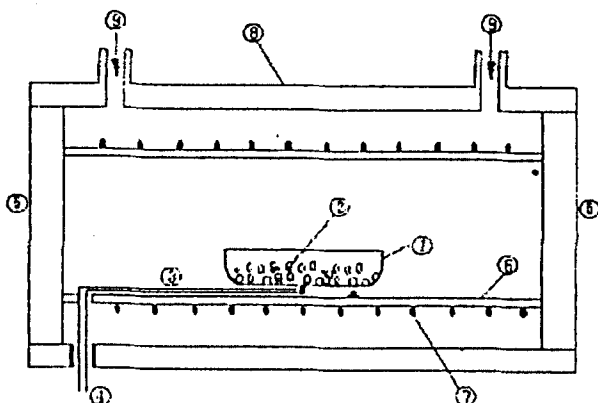


Fig. 2 'Heating decomposition cavity with semi-sealing' used for dynamic FT-IR, 1) platinum crucible; 2) sample; 3) thermocouple; 4) wire; 5) KBr crystal; 6) quartz tube; 7) heating wire; 8) shield; 9) heating wire introduction hole

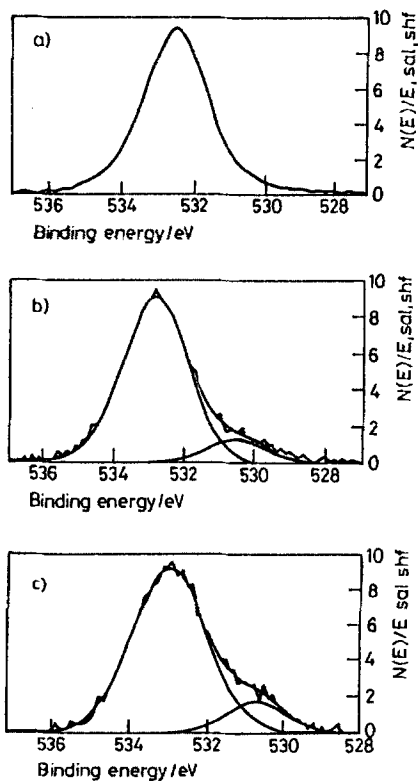


Fig. 3 XPS of O1s for different samples and curve fits, a) pure ethyl cellulose; b) EC adsorbed on superfine silver powder; c) EC adsorbed on shining silver powder

[7]. The O1s shift for EC before and after adsorption on silver means that the electron lone-pair of the oxygen is partially transferred to the silver atom, and a bond is formed between the oxygen electron lone-pair and the $5sp^3$ hybrid orbital of the silver.

DSC measurement

Figure 4 depicts the DSC curves of pure EC and superfine silver powder after EC adsorption, at a scanning speed of 10 K min^{-1} . This Figure reveals an obvious difference between these two thermal decomposition and oxidation processes. For pure ethyl cellulose, it is a slowly changing process in the entire temperature range, with an activation energy of 162 kJ mol^{-1} (curve A in Fig. 4). For ethyl cellulose adsorbed on superfine silver powder, it becomes two processes with activation energies of 104 kJ mol^{-1} (peak 1 in Fig. 4) and 135 kJ mol^{-1} (peak 2 in Fig. 4) respectively. (Using the Kissinger method of thermal reaction kinetics, shown in Fig. 5).

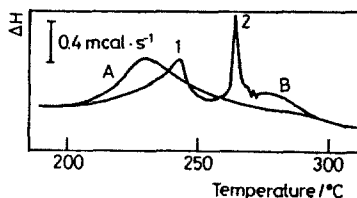


Fig. 4 DSC curves of thermal decomposition of different samples; A) film deposit of pure EC; B) EC adsorbed on superfine silver powder

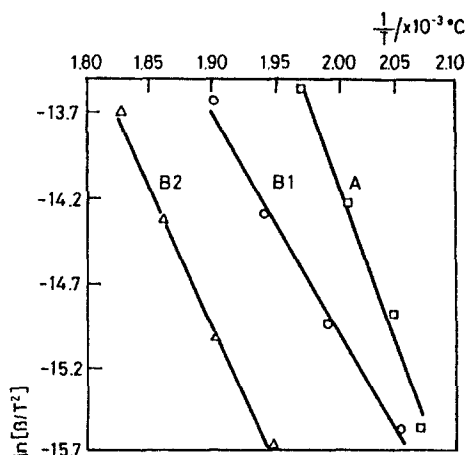


Fig. 5 The Arrhenius diagram for different samples; A) deposit of pure ethyl cellulose; B1) first peak of EC adsorbed on superfine silver powder; B2) second peak of EC adsorbed on superfine silver powder

For the film of EC, which is not affected by adsorption, the temperature of initial decomposition is lower than that for ethyl cellulose adsorbed on silver powder, but it has a high reaction activation energy: 162 kJ mol^{-1} . Ethyl cellulose adsorbed on silver powder decomposes into at least two parts during desorption and oxidation when this powder is heated. The decomposition therefore becomes a two-step process with lower activation energy.

FT-IR analysis

The FT-IR spectra of the decompositions of pure ethyl cellulose and ethyl cellulose adsorbed on silver powder are shown in Figs 6 and 7. There are C=O vibrations at around 1742 cm^{-1} . Since these are of low intensity and are strongly disturbed by the vibration of water vapor, we demolished the vibration spectra in the range $1350\text{--}1800 \text{ cm}^{-1}$. The quantitative changes in the decomposition and oxidation results are shown in Figs 8 and 9, in which the wavenumbers C-H: $2820\text{--}3000 \text{ cm}^{-1}$, C=O: $1685\text{--}1825 \text{ cm}^{-1}$, and C-O: $1025\text{--}1205 \text{ cm}^{-1}$ are used to calculate the integration of every cluster and the results have been normalized.

A comparison of these two Figures indicates that, when ethyl cellulose is adsorbed on silver powder, the C-O bonds are easily broken. This is because the C-O bonds are weakened when ethyl cellulose is adsorbed on silver powder. Thus, we

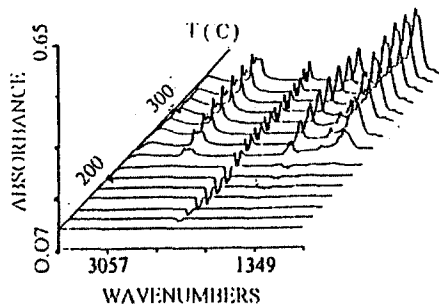


Fig. 6 FT-IR spectra of decomposition and oxidation of pure EC

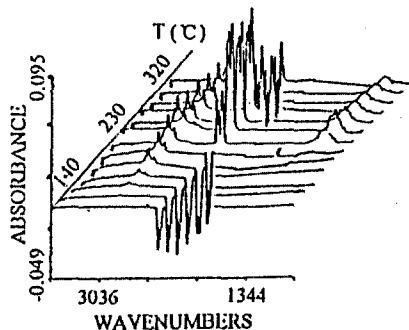


Fig. 7 FT-IR spectra of decomposition and oxidation of EC adsorbed on silver powder

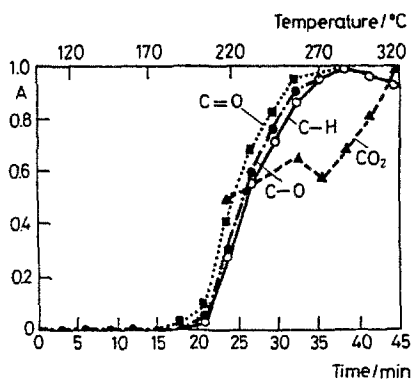


Fig. 8 Quantitative changes in the decomposition and oxidation results for pure EC

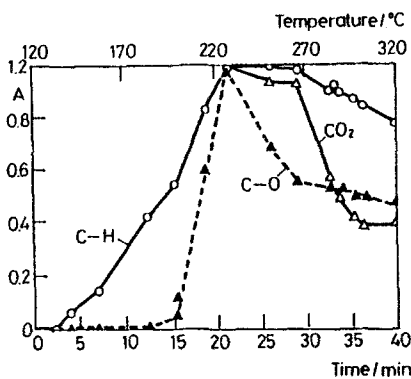


Fig. 9 Quantitative changes in the decomposition and oxidation of EC adsorbed on silver

can observe C-H fragments first when the sample is heated. With the increase of temperature, other clusters can then be observed. These results coincide with the double peaks on DSC analysis. As for pure ethyl cellulose, the decomposition products, including C=O, appear at almost the same time. This verifies the one peak in DSC experiments.

Conclusions

The above analyses suggest the following mechanism for the desorption and decomposition of EC adsorbed on silver powder:

A weak field 'bridge' is formed between the unoccupied $5sp^3$ hybrid orbital and the lone-pair electrons of oxygen atoms in ethylcellulose when they are adsorbed on superfine or shining silver powder. This leads to some C-O bonds being weakened or loosen. When the sample is heated, such bonds will break first and C-H fragments will be lost. With the increase of temperature, the C-O moiety will be oxi-

dized into C=O and leave the surface of the silver powder. This two-step process corresponds to the double peaks in DSC.

For pure adsorbed ethyl cellulose, there is no change in the bonds. No part of the ethyl cellulose has any priority to decompose and to be oxidized. This entire process takes place in a slow change mode and shows only one peak in DSC. The adsorption changes the decomposition and oxidation activation energy from 162 to 135 and 104 kJ mol⁻¹.

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