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Interaction of thin films of hydroxo-oxobis(8-quinolyloxo) vanadium (V) with ammonia vapour

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ABSTRACT

Hydroxo-oxobis(8-quinolyloxo) vanadium (V) organometallic complex has been prepared as thin films from dichloromethane solution by spin coating and the kinetics of its interaction with ammonia vapour is investigated using surface plasmon resonance (SPR) technique. Thin film parameters are deduced from SPR measurements as well as spectroscopic ellipsometry and UV–vis spectral absorption measurements. Initial exposure to ammonia vapour has resulted in a permanent change to the baseline of the measured kinetic response, which is explained by the formation of the ammonium salt of the complex. Further exposures to ammonia vapour after 24 h and beyond, are shown to be highly reversible, which can be ascribed to formation of hydrogen bonding of second ammonia molecule with the highly negatively charged ammonium salt of the vanadium complex. Exposures to other organic vapours such as ethanol, chloroform and benzene are also studied in order to examine the selectivity of this material to ammonia vapour.

1. Introduction

Ammonia gas is the key material for many important industrial processes in which it is used in a very high concentration. These applications range from steel and fertilizer manufactures to the refrigeration and combustion processes both in chemical plants and in motor vehicles. It is reported that 2.1–8.1 million tonnes of ammonia is produced annually in the atmosphere only from combustion processes [1]. However, there are still many little sources of ammonia such as the oceans and sea water surfaces by which ammonium ion (NH_4^+) usually exist [2]. There is therefore continuous demand to develop processes and materials, which can be used to selectively and reversibly identify the presence of this gas in the work place. A comprehensive review has recently been published by Timmer et al. which has discussed chemical and physical of ammonia detection [3].

The principle aim of this work is to examine and interpret the interaction of ammonia vapour with hydroxo-oxobis(8-quinolyloxo) vanadium complex (herewith abbreviated as OVQ_2OH) to produce ammonia salt adduct, and to monitor the reversibility of such interaction. In the present article, thin films of the organometallic vanadium complex OVQ_2OH are prepared for the first time, and the method of surface plasmon resonance (SPR) is used as the registration method to investigate the interaction between OVQ_2OH thin films and ammonia vapour. Since OVQ_2OH in solid phase has not been explored, especially in the field of chemical vapour monitoring, this may therefore lead to further investigation to identify the possible use of thin films of this material for ammonia detection, both at low and high concentrations.

It is well established in the literature [4] that hydroxo-oxobis(8-quinolyloxo) vanadium (V) chelate complex reacts irreversibly with vapours of aliphatic amines, alcohols or mercaptans in solution according to the following simplified chemical equation:

$$OVQ_2OH + RXH \rightarrow OVQ_2XR + H_2O \quad (1)$$

where XH is NH_2 in primary amines (or RNH in aliphatic secondary amines), OH in aliphatic alcohols and SH in aliphatic thiols. Little attention has been paid to the chemistry of OVQ_2OH in solution and in solid phase. The photochemistry of OVQ_2OH complex and its aliphatic alcohols and amines adducts has been studied for the first time by Aliwi and Bamford [5–8]. Furthermore the adducts of this complex proved to be effective photoinitiator of vinyl polymerisation at the radiation wavelength of $\lambda = 365$ nm at 25 °C [5–7]. It was also reported that photosensitive polymers are produced from the interaction of the OVQ_2OH complex with poly(hydroxyethyl methacrylate-co-methyl methacrylate) co-polymers [8]. OVQ_2OH was shown to possess semiconducting properties in the photofixation of carbon dioxide in the presence of methyl viologen and ethylene diamine tetraacetic acid dispersion electron relay system

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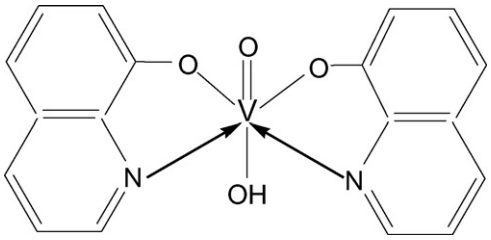

Fig. 1. Chemical structure of hydroxo-oxobis(8-quinolyloxo) vanadium (V) organometallic complex (OVQ_2OH).

[9]. Other transition metal chelates such as Zn [10], Ni [11] and Cu [12] phthalocyanines as well as 1-[(2-oxyphenyl)iminomethyl]-2-oxybenzene-*O*,*O*′,*N*′amine-nickel(II) [13] have been reported as ammonia, as well as organic vapour sensing membranes.

SPR has been widely suggested as a highly sensitive surface detection technique to monitor NH_3 molecules at low concentrations [12]. The SPR method has now become a well-established technique in the field of chemical [14] and biochemical [15] sensing applications. This method has been employed in the present work to investigate the interaction of ammonia with thin films of OVQ_2OH (see Fig. 1 for molecular structure) produced by spin coating form dichloromethane solution. Interaction of other vapours such as ethanol, benzene, hexane, chloroform and dichloromethane with OVQ_2OH films have also been examined for selectivity purposes.

2. Experimental methods

2.1. Chemicals

Hydroxo-oxobis(8-quinolyloxo) vanadium(V) complex is synthesised by adopting the modified procedure reported by Blair et al. [4] and as follows: 40 mmole of 8-hydroxy quinoline (QH) (Fisher chemicals, AR grade) was dissolved in 70 ml of 0.1 M acetic acid; to this solution, 20 mmole of ammonium metavanadate (Fisher chemicals GPR) dissolved in 100 ml of 1.0 M acetic acid at 70 °C, was added drop-wise. The reaction mixture was adjusted to a pH value of 5 with 2 M ammonium hydroxide. The formed black precipitate was filtered, washed with hot water, and dried under reduced pressure, and then washed with hot benzene. It was dried inside ambient air oven at 70 °C for 2 h. The compound is shown to be stable in air and humidity, insoluble in most of organic solvents except dichloromethane, in which it is stable for more than 6 months, and it is also slightly soluble in chloroform and *o*-dichlorobenzene. Dichloromethane (supplied by BDH (purity 99.5%) dried over molecular sieve before being distilled at atmospheric pressure) is used as solvent to prepare OVQ_2OH complex solutions. Ammonium hydroxide was used as a source of ammonia vapour and was supplied by Fisher Chemicals with 35% NH_3.

2.2. Film preparation

A 5 ml solution of 1.0 mg/ml OVQ_2OH in dichloromethane is prepared in ultrasonically clean 10 ml vial and placed in an ultrasonic bath for 10 min to ensure complete solubility. 0.1 ml of this solution was dispersed via a micropipette onto ultrasonically cleaned glass substrates held on a spinner (Microsystem 4000). The vanadium chelate solution was prepared by spin coating with spin speeds in the range 500–2000 rpm, for a period of 30 s. The dichloromethane has completely evaporated during this period leaving a reasonably homogenous dark violet film of OVQ_2OH despite the high evaporation rate of dichloromethane. The substrate material used was varied according to the experimental requirements for different characterization techniques. Glass slides coated with about 40 nm thermally evaporated gold films were used for the SPR measurements, while 100 (n-type) silicon wafers were used for ellipsometry measurements. The UV–vis absorption spectra were recorded for films spun onto ultrasonically cleaned glass slides.

2.3. Spectral and optoelectronic measurements

Optical spectroscopy and ellipsometry are used to study the optical properties of thin films of OVQ_2OH material. UV–vis spectra were recorded for the OVQ_2OH complex deposited on glass slides using Varian 50 Scan UV–vis spectrophotometer in the wavelength range 350–800 nm.

Ellipsometric measurements were performed on OVQ_2OH films spun onto silicon substrate using Woolam 2000V^{TM} rotating analyzer spectroscopic ellipsometer in the spectral wavelength range from 370 to 1000 nm. The angle of incidence was fixed at 60°. The dedicated software is used for data acquisition and analysis of the measured ellipsometric parameters $\Psi(\lambda)$ and $\Delta(\lambda)$ which are related by the following equation:

$$\frac{R_p}{R_s} = tan(\Psi)\exp(i\Delta) \quad (2)$$

where R_p and R_s are Fresnel reflection coefficients for p- and s-components of the polarized light related to the parameters of reflection system, particularly the thickness (d) and refractive index (n) of the deposited layers, via Fresnel equations [16]. SPR measurements are applied to study the interaction between OVQ_2OH and different concentrations of ammonia vapour mixed with ambient air. SPR measurements were carried out in a Kretschmann's type configuration [17], where films of OVQ_2OH spun onto Au-coated glass slides were brought in optical contact with the semicylindrical prism (with index of refraction $n_p = 1.515$) using ethyl salicylate (Aldrich 99%). Prism and sample combination was placed on a $\theta - 2\theta$ rotation table driven by microprocessor-controlled stepping motor (with resolution of 0.01°). The SPR excitation was obtained by focusing a p-polarized light beam of helium–neon monochromatic laser source (with wavelength $\lambda = 633$ nm) on to the prism/sample interface. A gas cell sealed at the sample through a rubber O-ring was employed to study the ammonia vapour interaction with the OVQ_2OH films. The kinetic response was studied by the injection of a known volume of ammonia vapour (using a gas tight syringe) taken from the vapour phase in equilibrium with the concentrated ammonium hydroxide solution. The desired concentration of ammonia was achieved by appropriate dilution with ambient air.

For kinetic measurements the intensity of the reflected laser light was recorded in situ for a fixed angel of incidence (θ^*) during the exposure with incremental pulses of NH_3 vapour concentrations. The angle θ^* was chosen to be very close to the SPR resonance angle, on the left side of the SPR curve minimum.

3. Results and discussion

Optical absorption spectral changes of OVQ_2OH thin films on exposure to saturated vapour of ammonia for a period of 5 min are presented in Fig. 2. It can be clearly seen that the broad band located within the range 550–650 nm (curve 1) shows significant decrease in the film absorption on exposure to ammonia. This band is known to be due to charge transfer from the OH group to the vanadyl group (V=O) [18]. The disappearance of this absorption band on exposure to ammonia (see curve 2) is ascribed to the formation of ammonium