



Determining Surface Vinyl on Vinyltriethoxysilane Modified Nanosilica by Coulometry

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(Received: 29 April 2010;

Accepted: 12 January 2011)

AJC-9468

A coulometric method to determine surface vinyl on vinyltriethoxysilane modified nanosilica (VTES-SiO₂) quantitatively was established. The influences of electrolyte, reaction time, compensation polarization potential, solvent *etc.* in the determination system were studied. Experimental results indicated that the optimum conditions was to adopt the system of 50 mL 2 mol/L KBr + 300 mL HCOOH + 150 mL anhydrous ethanol as electrolyte, 0.5 h of reaction time, 250 mV of compensation polarization potential. This method was precise and accurate with recovery ratio of 98.1-103.3 % and relative standard deviation of 2.16 %. It might be used to determine surface vinyl on VTES-SiO₂ and its relevant products.

Key Words: Vinyl, Vinyltriethoxysilane, Nanosilica, Determination, Coulometry.

INTRODUCTION

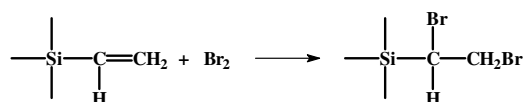
Functional materials is a key area of new materials' field research and development in the 21st century throughout the world, also, the hot point of strategic competition in the global high-tech development. With double-function structure¹, vinyltriethoxysilane (VTES) can combine with inorganic materials and can react with organic materials, is a fine functional modifier of SiO₂. Nano-SiO₂ modified by VTES (VTES-SiO₂) is well hydrophobic. The number of hydroxyl makes considerable reduction and the interacting force between particles is much weakened, making reunion action greatly improved. Therefore, VTES-SiO₂ has a wide range of applications in the field of rubber², glass³, medicine⁴, membrane materials⁵, ceramics⁶, composite materials⁷ and biology⁸.

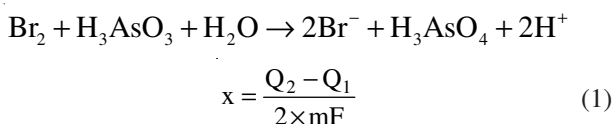
The content of VTES on the surface of VTES-SiO₂ can be determined by the content of double bond in it, which are based on special reaction of double bond, such as mercuric acetate, iodometric methods *e.g.*, volumetric analysis and colorimetry⁹ and chromatography. However, there are two issues which are easily to be neglected in capability analysis, one is the exact determination of the contents of benchmark substance and the volume of titrant¹⁰, the other is the strong adsorption of VTES-SiO₂ to indicator. Franc¹¹ reported that ethylene in non-dissolving organic silicon compound can be determined by molybdenum reagent colorimetric estimation. However, it is difficult to handle and easy to introduce error, because

pyrolysis takes place in NaOH environment and ethane should be collected exactly. Moreover, it is difficult to determine by chromatogram for the time being. Therefore, a constant-current coulometric method to detect the amount of double bond on VTES-SiO₂ is established and electrochemistry capability influencing electric current efficiency, electrode action of electrolyte and other factors influencing determination are investigated systematically, an optimum reacting condition is established. Sample analysis and recovery ratio determination show that this method has a high degree of accuracy and precise.

EXPERIMENTAL

VTES-SiO₂ has active groups those double bonds, which can react with Br₂, quantitatively. So VTES-SiO₂ was reacted with superabundant Br₂ in CCl₄ and residual Br₂ was removed by excessive As(III) standard solution. Then the residual As(III) was determined by coulometry through reaction with generated Br₂ on Pt electrode. When the sample and reagent blank experiments were carried, the electric quantity Q₂ (sample electrolytic electric quantity) and Q₁ (blank electrolytic electric quantity) were obtained. Thus the amount of double bond on VTES-SiO₂ surface was calculated. The reactions and formula were as follow:





where x is the amount of double bond in sample (mmol/g); m is the mass of sample added (g); F is Faraday constant (96485C/mol).

Vinyltriethoxysilane (VTES) was produced by Bai Ling Wei Company with 99.5 % of purity. VTES-SiO₂ (Sample B and C), industrial products, were prepared by Henan Province Nanomaterial Engineering and Technological Research Centre. All the other reagents were analytical grade and high purity water was used throughout.

As(III) standard solution: 0.1400 g As₂O₃ was first dissolved with 5 mL 20 % NaOH and then taking phenolphthalein as indicator, used 1 mol/L sulfuric acid to neutralize the solution until achromatism and 10 mL excessively, Finally, the mixture was diluted by water to 1000 mL. As(III) concentration was 1.412×10^{-3} mol/L.

Br₂-CCl₄ solution: 0.0167 g KBrO₃ was dissolved with 1 mL 2 mol/L KBr and some drops of HCl, immediately, there emerges yellow smog from solution, producing pungent bromine. Put into appropriate amount of CCl₄ solution right away to extract 3 to 4 times, then is diluted by CCl₄ to 500 mL. Br₂ concentration was about 6×10^{-3} mol/L.

Electrolytes: **A**, 150 mL CH₃OH + 50 mL of 2 mol/L KBr + 300 mL CH₃COOH; **B**, 150 mL CH₃OH + 50 mL 2 mol/L KBr + 300 mL water; **C**, 150 mL HCOOH + 50 mL 2 mol/L KBr + 300 mL water; **D**, 50 mL 2mol/L KBr was diluted to 500 mL with water; **E/F/G**, 50 mL 2 mol/L KBr + 300 mL HCOOH + 100/150/300 mL anhydrous ethanol.

All experiments were performed on a KLT-1 current Coulomb-meter (Jiangsu Electroanalysis Instrument Factory) with platinum plates as electrodes (50 mm²). 50 mL electrolyte and 1 mL H₂SO₄ were added into electrolytic cell and a little of the mixture was poured into cathode cell to pre-electrolysis by proper electric current. Then 1 mL of the original Br₂-CCl₄ solution or the sample (weighted certain amount VTES-SiO₂ and reacted with 5 mL Br₂-CCl₄) for 0.5 h in dark and 5.00 mL of As(III) standard solution were added into electrolytic cell. After all was ready, start Coulomb-meter until indicator light shined. Record the Q_1 and Q_2 . Thus the vinyl on VTES-SiO₂ was calculated by eqn. 1. As for the conditions discussions, VTES-SiO₂ was instead by reference VTES throughout.

RESULTS AND DISCUSSION

Efficiency of electric current: Taking a certain amount of reference VTES standard solution in CCl₄, the electric quantity was consumed as 504.2 mC with electrolyte F. The theoretical consumed electric quantity was 504.5 mQ according to Faraday law. It indicated that the efficiency of electric current was amount to 99.94 %, confirmed the feasibility of the method.

Selection of electrolyte: As one of the weaker oxidants, Br₂ didn't demand generator anode with high potential like chlorine or weren't easy to cause oxidation of platinum electrode and water's oxygenation. Therefore, the efficiency of

electric current of generating chlorine on platinum electrode could reach 100 % as titration continuing. Because generating Br₂ was used in the present work, electrolyte needed salt with bromine ion and supporting electrolyte should be acidic, hence, coulomb titration was carried out in an acidic medium (pH < 5), to avoid dismutation of Br₂ when pH was > 5.

When electrolytes **A, B, C, D, E, F** and **G** were taken into experiments, results were showed that, when electrolyte **A** was used, reproducibility was bad, which might result from substitution reaction between Br₂ and hydrogen of methyl group in glacial acetic acid. When electrolytes **B, C** or **D** were used, there were white oil thickness forming as Br₂-CCl₄ being added into, which might be attributed to the large proportion of water in electrolyte that could not dissolve CCl₄ friendly, at the same time, the turbidity could be adsorbed onto electrode surface leading to insensitive end-point; when electrolyte **E** was used, rising velocity of electric quantity was slow and end-point was insensitive. In case of electrolyte **F**, the change of electric quantity was fast with sensitive end point and repeatable results. Good results were also obtained when electrolyte **G** was used, but it was uneconomical. Thus electrolyte **F** was selected as electrolyte.

Selection of compensation polarization potential (CPP): According to experimental methods, effect of CPP was investigated by determining reference VTES. As shown in Fig. 1, when CPP was above 150 mV, results were got with better reproducibility and stability. So CPP should be higher than 150 mV. At present work, 250 mV was used.

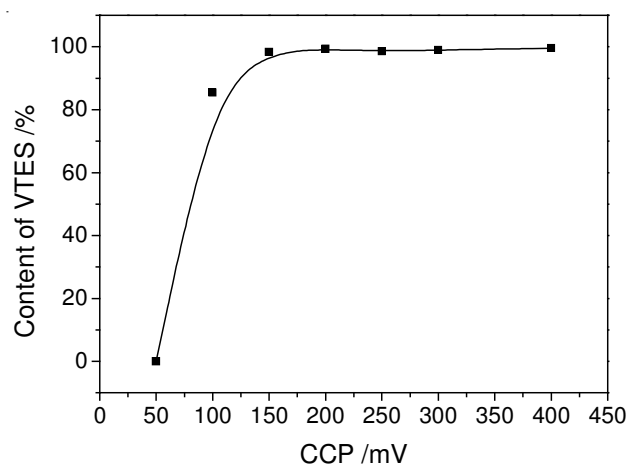


Fig. 1. Influence of compensation polarization potential (CPP) on determination of VTES

Selection of reaction time: Reaction time was confirmed by reacting reference VTES with Br₂ in CCl₄. Results were shown in Fig. 2. As shown, the content of VTES was determined as 99.6 ± 0.15 % which was closed to the theoretical content 99.5 %, when the reaction time was at 30 ± 3 min. Whether the time was lower than 27 min or higher than 33 min, the content of VTES was not obtained in accord with the theoretical one. It might be attributed that when the time was lower than 27 min, the reaction was incomplete and, when the time was higher than 33 min, VTES would hydrolyzed and the products could react with Br₂ and Br₂ also would be volatilized. So reaction time was confirmed as 30 min.

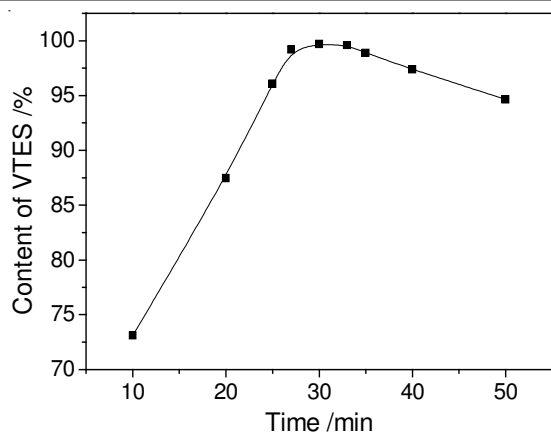


Fig. 2. Influence of reaction time on determination

Determination of sample and recovery ratio: According to experimental methods, the contents of double bonds in sample **B** and **C** were determined. Results were listed in Table-1. As shown, the relative standard deviations (RSD) were under 5 % for the determination method. It indicated that the method had a high degree of precision. The recoveries of reference VTES with sample **B** were also carried out. Results were listed in Table-2, with the recoveries of reference were between 99.5 and 102.4 % and RSD was 2.16 %. It suggested that the method was accurate and could be used for determination double bond on these kind nanoparticles.

TABLE-1
RESULTS OF SAMPLE DETERMINATION

Sample	Sample content (mmol/g)					Average (mmol/g)	RSD (%)
	0.2549	0.2587	0.2657	0.2680	0.2689		
B	0.2549	0.2587	0.2657	0.2680	0.2689	0.2598	2.33
C	0.0340	0.0334	0.0350	0.0345	0.0372	0.0348	4.18

TABLE-2
DETERMINATION OF RECOVERY RATIO

Sample	Recovery ratio (%)					Average (%)	RSD (%)
	102.4	99.7	99.5	98.1	103.3		
B	102.4	99.7	99.5	98.1	103.3	100.6	2.16

Conclusion

Coulometry method has been established for determining vinyl on VTES-SiO₂. It was found that the electrolyte, reaction time, compensation polarization potential were the key factors that affected results. The system of 50 mL 2 mol/L KBr + 300 mL HCOOH + 150 mL anhydrous ethanol was found to be a good electrolyte for the determination, as well as, 0.5 h of reaction time and 250 mV of CPP were found to be optimum operation conditions. The method was used for determination of vinyl on VTES-SiO₂ with good preciseness and accurateness. The recoveries of reference VTES were found to be between 98.1 and 103.3 %. This established method could be used for determining vinyl on VTES-SiO₂ and other relevant particles.

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EUROANALYSIS XVI

11 — 15 SEPTEMBER, 2011

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