A study on the preparation and application of Ag/TiO₂ complex sol-part 1: Preparation and properties of Ag/TiO₂ complex sol

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ABSTRACT

The primary aim of this study is to explore the property of Ag/TiO₂ complex sol. Ag/TiO₂ complex sols are prepared at different pH values. The results show that the reaction of Ag and Ti(OH)₄ is not suitable for the generation of Ti-O-Ag under alkaline conditions. Dried complex sols formed under acid conditions have a smaller particle size, whereas dried gels formed under alkaline conditions present a laminated structure. With increasing concentration of AgNO₃, specific surface area and pore volume of the dried gel are larger, but the orifices become smaller. In the case of excess AgNO₃, for example 4-10 dried gel, there is a reverse effect on particle size.

INTRODUCTION

The gel method is a chemical method in which a metal or semi-metal alkoxysilane is subjected to hydrolysis and polycondensation. In this technology, an inorganic precursor is used with acid-base catalysts to generate reticular compounds. This technology makes it possible for processing at low temperatures, and organic materials can be incorporated into the inorganic phase without decomposition. This method allows the preparation of many products, such as powder, gel, dried gel, fiber and coatings. The gel method allows the metal oxide of functional groups to be coated onto various materials, serving the purpose of surface modification; for example: glass, metal or organic high polymers.

Once made use of a sol-gel method to make compound photo-catalyst in the past research paper, by with amplification TiO₂ it stirred up a wave-length, but for applied compound sol in fabrics of the dying and finishing of research not much, so this research will synthesize various compound sol and make into dry gel and discuss a making the condition is to the related property of the sol or the dry gel, with is used as the reference that the follow-up appliance processes.

EXPERIMENTAL

Materials

Titanium n-butoxide (99%, TTB); ethyl alcohol, acetic acid, nitric acid, sodium hydroxide, hydrochloric acid, were purchased from Shimahisashi Pharmaceutical; ethyl acetoacetate (EAc) was purchased from NIHON SHIYAKU INDUSTRIES; silver nitrate was purchased from Wako Pure Chemical Inc. Ltd.
METHODS

Preparation of complex sol

With vigorous stirring 10ml of butyl titanate (TTB) was added to 30ml of absolute ethyl alcohol, and then 2ml of acetic acid and 0.2ml of acetylacetone were added. After stirring for 30 minutes, a uniform and transparent solution was obtained (solution A). Distilled water (1ml) was slowly added to 15ml of ethyl alcohol, and 0.1ml of 1M nitric acid was added slowly, then the mixture was stirred for 30 minutes to obtain solution B. By adding solution B slowly into solution A, it was possible to obtain a uniform and transparent yellowish sol. After stirring for 1 hour, 40ml of distilled water was added to produce a white sol. At different pH values (2~10), the TiO_2 sol at the concentration specified above was added to a solution of AgNO_3, thus forming a reaction system. Stirring was continued for 3 hours to obtain the Ag/TiO_2 complex sol. Next, an Ag/TiO_2 dried complex sol was prepared by drying the sol for 2 hours at 80°C, then the dry gel were wash with distilled water until to neutralize.

Analysis and measurement

Fourier transform infrared spectroscopy in the attenuated total reflection mode (FT-IR/ATR) spectra of the dried gels was recorded with a Bio-Rad Digilab FTS-200 spectrometer using an MCT detector. A diamond crystal was used as the internal reflectance element. Single-beam spectra were the result of 64 scans. The spectral resolution was 4 cm\(^{-1}\). The surface morphologies of the films were observed with a JEOL model JSM 6400 scanning electron microscope. A gold coating was deposited onto the samples to avoid charging the surface. The distributions of all atoms of the Ag/TiO_2 dried gels were analyzed by energy-dispersive X-ray spectroscopy (EDS; model EDSEM, JEOL, Tokyo, Japan). A Bruker-AXS D8 was used for X-ray powder diffraction (parallel beam optics, Cu-target, scintillation counter, sampler changer with rotation). The samples were run with 40 kV, 100mA, 5-60°/2θ, 0.01° stepsize and 5 sec counting time. The surface area and pore volume of the dried samples were determined through nitrogen physisorption analysis, using a Quantachrome Autosorb-1 system. The five-point BET calculation was used to determine the surface area.

RESULTS AND DISCUSSION

FT-IR

To analyze the property of various sols, Ag/TiO_2 dried complex sol was prepared by drying the sol for 2 hours at 80°C. Figure 1 depicts FT-IR spectra of Ag/TiO_2 dried complex sols prepared at different pH values. Among dried gels of 1380 cm\(^{-1}\) and 1625 cm\(^{-1}\), absorption peaks of Ti-O-Ti and >C = O groups are clear, of which >C = O is represented by the >C = O absorption peak of a compound of Ag and ethyl acetylacetone. In figure 1a-D, there is obviously a C = C absorption peak at 1540 cm\(^{-1}\). It can thus be proved that, although AgNO_3 is likely to form AgOH under
alkaline conditions, it is unlikely to react with Ti (OH)₄ to generate Ti-O-Ag after polycondensation. This can be deduced from an obvious O-H absorption peak at 3442 cm⁻¹. But, no obvious difference exists in figure 1b-A to 1b-C.

**SEM and EDS**

As illustrated in figure 2, the particle sizes of dried complex sols increase with increasing pH, and TiO₂ is made available at the white section. The particles are slightly bigger, since silver nitrate readily forms silver hydroxide under alkaline conditions, which is easily adhered to the surface of TiO₂. Secondly, the appearance of the dried gel differs a little, due to different concentrations of silver nitrate. As illustrated in figure 2, when the concentration of silver nitrate becomes higher, the silver component in the dried gel increases (the black part) with a decreasing amount of TiO₂ (the white spot). By comparing the acid-base of 2-c and 2-d, acid Ti (OH)₄ is easily bonded with Ag in the compound, thus forming Ti-O-Ag of smaller particles. Conversely, alkali AgOH presents a laminated structure due to larger

![Figure 3: EDS of Ag/TiO₂ dry gel. (a): 4-10, (b): 6-10](image)

![Figure 2: SEM of vary Ag/TiO₂ complex dry gel. a): 4-1, b): 4-6, c): 4-10, d): 6-10, e): 10-10](image)

**TABLE 1: Various signs of complex sols are defined below**

<table>
<thead>
<tr>
<th>Sign</th>
<th>Definition</th>
<th>Concentration of AgNO₃ (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>Complex sol prepared with 1ml of AgNO₃ at pH 4</td>
<td>5.7×10⁻⁵</td>
</tr>
<tr>
<td>4-3</td>
<td>Complex sol prepared with 3ml of AgNO₃ at pH 4</td>
<td>1.71×10⁻⁴</td>
</tr>
<tr>
<td>4-6</td>
<td>Complex sol prepared with 6ml of AgNO₃ at pH 4</td>
<td>3.42×10⁻⁴</td>
</tr>
<tr>
<td>4-10</td>
<td>Complex sol prepared with 10ml of AgNO₃ at pH 4</td>
<td>5.7×10⁻⁴</td>
</tr>
<tr>
<td>6-10</td>
<td>Complex sol prepared with 10ml of AgNO₃ at pH 6</td>
<td>5.7×10⁻⁴</td>
</tr>
<tr>
<td>8-10</td>
<td>Complex sol prepared with 10ml of AgNO₃ at pH 8</td>
<td>5.7×10⁻⁴</td>
</tr>
<tr>
<td>10-10</td>
<td>Complex sol prepared with 10ml of AgNO₃ at pH 10</td>
<td>5.7×10⁻⁴</td>
</tr>
</tbody>
</table>
A study on the preparation and application of Ag/TiO$_2$ complex sol

**CONCLUSIONS**

This study has prepared Ag/TiO$_2$ complex sol at different pH values. The objective was to explore the property of dried complex sol. The following conclusions are drawn from the test results. (1) Dried complex sols prepared under acid conditions have smaller particles, whereas those prepared under alkaline conditions present a laminated structure. The relative weight percentage of Ag in the dried gel decreases with increase of pH value. (2) The concentration of AgNO$_3$ has an influence upon the weight percentage of dried complex sols but not on the crystal structure. The acid-base conditions have no influence upon the crystal structure of the dried gel. (3) In the case of increasing concentration of AgNO$_3$, specific surface area and the pore volume of the dried gel was increased, but the orifice size becomes smaller. In the case of an excessive amount of AgNO$_3$, there is a reverse effect on particle size. Under alkaline conditions, the dried gel presents the largest aperture but the smallest specific surface area and orifice volume.

**REFERENCES**