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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
14 OCT 93

3. REPORT TYPE AND DATES COVERED
Technical Report, 01 JUN 93 - 31 AUG 93

4. TITLE AND SUBTITLE

Crystallization of silver chromate from ethanol via salt metathesis reactions of solubilized precursors

5. FUNDING NUMBERS

6. AUTHOR(S)

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FEB 2 1994
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8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report No. 7

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

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12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Admixture of aqueous solutions of silver nitrate and potassium chromate results in immediate precipitation of silver chromate as a red-brown microcrystalline powder, while addition of aqueous silver nitrate solution to a solution of potassium chromate/18-crown-6 in ethanol gives a bright-red precipitate. X-ray powder diffraction shows both materials to be orthorhombic silver chromate. The ethanol-derived sample displays broader diffraction peaks, suggesting smaller crystallite size. Scanning electron microscopy confirms this. The ethanol-derived sample appears amorphous, while the aqueous sample displays well-faceted crystallites approximately 0.5 - 1 micron in size.

14. SUBJECT TERMS

Nonaqueous crystallization; complexation-mediated crystallization

15. NUMBER OF PAGES
2

16. PRICE CODE
N/A

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
UL

NSN 7540-01-280-5500

Standard Form 298 (Rev
Prescribed by ANSI Std Z39
298-102

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1731

R&T Code 413p010---03

Technical Report No. 7

Crystallization of silver chromate from ethanol via salt metathesis reactions of solubilized precursors

by

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Interim Technical Report

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October 14, 1993

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Experimental

Two samples of silver chromate (Ag_2CrO_4) were prepared by admixture of solutions of $AgNO_3$ and K_2CrO_4:

Sample A: $AgNO_3$ solution in water added dropwise to solution of K_2CrO_4 in water, resulting in immediate precipitation of a red-brown powder. This was isolated by filtration and washed with water, then ethanol, then diethyl ether, affording the Ag_2CrO_4 as a brown powder in high yield.

Sample B: $AgNO_3$ dissolved in 0.5 mL water, then diluted with 4 mL ethanol and added dropwise to a solution of K_2CrO_4 in ethanol (6 mL) containing 3 equivalents of 18-crown-6, resulting in immediate precipitation of a red powder. This was isolated by filtration and washed with ethanol, then water, then ethanol, then diethyl ether, affording the Ag_2CrO_4 as a red powder in high yield.. (Note that K_2CrO_4 appears completely insoluble in ethanol in the absence of 18-crown-6.)

Each sample was examined by x-ray powder diffraction and shown to be the (known) orthorhombic phase of Ag_2CrO_4. Each appeared crystalline; however, sample A (prepared from water) appeared to be composed of significantly larger crystallites, as evidenced by sharper lines in the powder diffraction pattern.

Scanning electron microscopy confirmed this observation: Sample A was comprised entirely of apparently well-faceted crystallites approximately 0.5 - 1 micron in size, while sample B displayed no clearly identifiable crystallites, being composed instead of aggregates of visually amorphous (but, recall, still crystalline as shown by x-ray powder diffraction) material.

Discussion

Silver chromate serves an important role as a cathode material for nonaqueous-electrolyte batteries. It has also appeared in the patent literature as an alkene polymerization catalyst, as a potential optical recording material, and as a component in anti-fouling agents. It is generally prepared by a simple metathesis reaction between, e.g., potassium chromate and silver nitrate. Such metathesis reactions are universally carried out in aqueous solution, as the precursors display negligible solubility in nonaqueous solvents. We have found that use of 18-crown-6 as a complexing agent allows preparation of solutions of potassium chromate in ethanol. Dropwise addition of ethanolic silver nitrate (containing a few percent water in order to solubilize the silver salt) to such an ethanolic solution of solubilized potassium chromate results in immediate precipitation of silver chromate which, as demonstrated by visual inspection (color of the bulk sample), X-ray powder diffraction, and electron microscopy, is of significantly smaller crystallite size than silver chromate prepared from aqueous solution. The ability to effect such a significant alteration in crystallite size simply through alteration of crystallization medium, made possible through application of our technique of complexation-mediated crystallization, may prove of profound importance in, e.g., the area of semiconductor nanoparticle technology.