Commun. Fac. Sci. Univ. Ank. Series B
V. 49. pp.5 - 14 (2003)

SYNTHESIS AND CHARACTERIZATION OF A NEW COBALT POLYMERIC SPINELS

SHAEEL A. AL-THABAITI

Chemistry Department, Faculty of Science, King Abdulaziz University, P.O.Box 80203, Jeddah 21585, Saudi Arabia

Received: Oct.10,2003; Revised: Dec.18,2003; Accepted: Dec.23,2003

ABSTRACT

Some cobalt spinels were synthesized under hydrothermal conditions, starting from metal chlorides, and Poly N-Acrolylquinazoline. The color properties in these systems mainly depend upon the preparative method and cation distributions, which have been determined by visible and near infrared absorption spectra. We observe the influence of tetrahedral and octahedral preference of cations such as Co^{2+}, Cr^{3+}, Mn^{3+} upon the formation and the color development of cobalt spinel polymers. All the samples prepared revealed the formation of single spinel with particle size at about 0.8-2.1 μm; $CoAl_2O_4$ reveals kings blue, $CoMn_2O_4$ dark blue and $CoCr_2O_4$ bluish green. Cobalt blues developed giving deep absorption characteristic of tetrahedral Co^{2+} ions at about 550-680 nm; therefore, color changed from kings blue to bluish green in $CoCr_2O_4$, showing the absorption band of octahedral Cr^{3+} ions owing to the large excess octahedral crystal field stabilization energy.

Key words: Hydrothermal (TGA and XRD), Spinels, Acrolylquinazoline

1. INTRODUCTION

In recent years there has been increasing interest in the synthesis of nanocrystalline metal oxides. Oxide spinels are important for a variety of applications including magnetic materials, refractoriness and superconductors materials. Oxide spinels are refractory oxide materials with optical properties, highly applicable in chemical industries as ceramic pigments and as anticorrosive heat resistant coatings (1,2). Color is an important characteristic of many ceramic products such as dinnerware, tile, porcelain enamels, sanitary ware, some glasses and structural clay products. Ceramic pigments are presently classified either according to their colors or their crystal structures. These classification do not give microscopic information such as chemical states of coloring ions; thus, it seems still safe to say that the manufacture of ceramic pigments is based on empirical knowledge.

In the designing of novel ceramic colors, it is desirable to know about the chemical states and behaviors of coloring elements. The microscopic view is essential for synthesis of new color as well as for the modification of colors of conventional ceramic pigments. There are two properties of any ceramic pigment, which are most important, stability and tinctorial strength. The latter is not only a matter of intensity of color, but also of brightness. The other important property of a ceramic color is stability under high temperatures and corrosive environments encountered in the firing of glazes and enamels. These requirements limit ceramic colors to a very small number(3). We chose spinel becaue they withstand high temperatures (=2000°C) and an aggressive environment. The spinel structure, which has the general formul AB_2O_4 consists of an almost perfect cubic close packed oxygen arrangement in which the cations roside on tetrahedral and octahedral interstices. The structure presents 64 tetrahedral or A sites and 32 octahedral or B sites of which only 8 and 16 are occupied respectively, by cations in the stoichiometric spinel.

In the normal spinel, A ions are located in tetrahedral sites, whereas in the ideal inverse spinel, they are located in octahedral sites. The majority of spinels show some degree of disorder. Any intermediate partly disordered state may be expressed as a mix of these two end members with a general formula $(A_{1-x}B_x)$ $[B_{2-x}A_x]O_4$, where x is the inversion parameter. Thus, the inversion parameter is the fraction of tetrahedral sites occupied by trivalent cations. The behavior of the 3d electrons of the transition metal ions in these structures may be treated by crstal field model(4).

The aim of this paper is to develop low temperature route for the production of new stale, consistent, low cost and high intensity of non crystalline (1-3 μm) cobalt blue. In this route aqueous solutions were preferred due to the ease of handling, safety, low cost and availability of a wide range of water soluble salts. We use metal chlorides because they have the highest water solubilities relative to other metal salts.

Experimental Preparation

Sample Polymer Preparation

The spinel precursors were prepared by Co precipitation from an alkaline solution(6). The process involved dissolution of metal chlorides and Poly N-Acrolyquinazoline in aqueous solution. $CoAl_2O_4$ was prepared from a solution of 1 M $CoCl_2$ to which was slowly added a solution of 2 M $AlCl_3$ with stirring and at a temperature of about 90 °C. To this mix, 1.75 M of ammonia was added slowly to control the pH ot the solution and to obtain a rose precipitate at pH values of 8.25+0.25. The precipitated solid product was separated, washed with distilled water to remove chloride ion, dried, and calcined in electric furnace at 700 °C for 3 h. For the other pigmens the procedure is the sane, with $CrCl_3$ and $MnCl_3$.

UV-V-IR (near) spectrophotometer

In order to determine the environment of the cations in these structures and the color propeties, the corresponding diffuse reflectance spectra of the samples were obtained from a Cary/Varian 177 grating spectrometer optimized for the near infrared.

X-ray diffraction

The structure of the polymers (pigments) was determined by the X-ray powder diffraction using CuKd radiation in a D5000 siemens diffractometer. Diffraction intensity was measured in the 2Θ range between 2.5 and 70°, operating at 35Kv and 25mA. The crystallite size of the powder pigment is calculated from XRD line broadening using Scherrer's equation (King and Alexander 1974). Crystalline structure and cation distribution were refined with the rietveld technique by using DBWS program (Young et.al, 1995). Diffraction intensity was measured in the 2Θ range between 20 and 120°, with a 2Θ step of 0.02 for 6s per point.

Thermal analysis

Thermogravimetric TG measurement were made using Perkin-Elmeranalyzer TGA-7 attached to a proferrional computer 7700 in an inert atmosphere. Sample 7 mg were heated at 10 °C min^{-1} in dynamic nitrogen.

Electron microscopy

Morphology of the pigment particles were carried out on a JEOL scanning electron microscope (SEM, JE M6100) operating at 20 kV.

Results and discussion

These polymers were obtained in unique phase. The chemical process starts from the homogeneous distribution of metal ions in solution. The cation of metals attract the dipolar water molecules with which they build solvated units. In the precipitated insoluble salts like hydroxides, oxalates, acetates(7). The steps in the synthesis of $CoAl_2O_4$ can be summarized by the following type of reactions:

$$CoCl_2(aq) + AlCl_3(aq) + NH_4OH \longrightarrow$$

$$X\ Co(OH)_2.y\ Al\ (OH)_3 + NH_4ClxCo(OH)_2.y\ Al\ (OH)_3$$

$$\longrightarrow\ CoAl_2O_4$$

The values of x and y are usually quite complex functions of pH.

The XRD studies and micrographs (SEM) of the calined powders have revealed that crystallization of the powder begins above 500 °C and at 60 °C. The spinal crystallize completely with an average crystalline size of the order. 0.8-2.1 μm. The XRD patterns of the calcined powders for there pigments are shown in Fig.(1); we observed the single spinel in each case and its possible identification.

The studies of micrographs$^{(8)}$ (SEM) of the calcined powders have revealed that crystallization of the powder begins above 500 °C and at 600 °C the spinel crystallize completely with an average crystallite size of the order 0.8-2.1 μm. Structural refinements were carried out using the program DBWS for which a pseudo voigh profile was used. We assumed space group Fd3m with complete occupancy of 8 (a) and 16 (d) sites by cations, with oxygen in the 32 (e) sites, such model is in excellent agreement with extensive single crystal refinements on other spinels*. Refined Fig.2 parameters were: the lattice parameter a°, the inversion parameter x, and the oxygen positional parameter, u. The results from the Rietveld refinements for the three pigments are reported in Table (I). The main external constraint on judging the accuracy of these refinements is the crystal-chemical expectation that x should be zero. In the model of O'Neill$^{(9)}$ and Navrotsty. The cation distribution in a simple oxide spinel of formula AB_2O_4 where A and B could be Co^{2+} and Cr^{3+}/Co^{2+} and Mn^{3+}/Co^{2+} and Al^{3+} is described by the general equation:

$$\text{In}\left[\frac{x^2}{(1-x)(2-x)}\right] = \left[\alpha^{A-B} + 2\beta x - T\sigma^{A-B}\right] / \text{RT}$$

The term in the parentheses on the left hand side is the equilibrium constant for the cation distribution reaction. The quantity α^{A-B} is the difference in the site preference energies of A and B. The site preference energies of a cation in a spinel is determined by a number of factors including its ionic radius in both Tetrahedral and octahedral coordination, and the difference in its crystalline field stabilization energies (CFSE) in tetraheral and octahedral coordination. α^{A-B} is an entropy term, introduced to account for any non-configurationally entropy of disordering, and is expected to be relatively small. The term β in the model is taken to be the same for all 2-3 spinels. The large excess octahedral CFSE of Cr^{3+}

(=-160 kJ/mol) should ensure that the chromite spinel had an almost completely normal cation distribution.

Table 1. Synthesis temperature, refined parameter, size particles and color

Spinel polymers	**Synthesis temperature °C**	**a° (A)**	**U**	**X**	**Size particle (μ m)**	**Color**
$CoAl_2O_4$	700	8.0910	0.2642	0	1.2	Kings blue
$CoCr_2O_4$	700	8.352	0.2640	0	0.8	Bluish green
$CoMn_2O_4$	700	8.3457	0.2698	0	2.1	Dark blue

Also in the case of the manganite spine, the CFSE of Mn^{3+} (150.2 kJ/mol) should ensure the same(11). The results of the structural refinements show that X is effectively zero for all three pigments. The small increase in a° is consistent with the increase in mean effective ionic radii of trivalent cations Al, Cr and Mn (0.57, 0.70 A° respectively). From crystal chemistry considerations these spinels are expected to have an almost completely normal cation distribution (10). Figure (2). The polymer used as masking for each ions to insure completely homogeneous mixed metal ions. In $CoAl_2O_4$, the Al^{3+} ion is not a transition metal and only the Co^{2+} ion determines the occupation site in the crystalline structure. Co^{2+} lie in tetrahedral and trivalent cations in octahedral the structure is described like strings of edge-sharing octahedral, parallel to each other on the same level and perpendicular on adjacent levels and are joined by edge-sharing. Co^{2+} ions lie in tetrahedral between these strings, the tetrahedral and octahedral being joined only by corner-sharing(11) . The spectrum of reflectance diffuse, obtained in the visible (400-700 nm), near infrared (750-2,500 nm), and ultra-violet (300-400 nm), regions, originate from three types of electronic transition process: crystal field d-d or intra-electronic transitions, metal-metal intervalence transitions and oxygen-metal charge transfer(12). Crystal field spectra originate when electrons are excited by light between incompletely filled 3d orbital energy levels within the transition metal ion, like in these spinel pigments. The crystal field contribution for spinels can be assessed by considering the difference in crystal field stabilization energies for octahedral compared to tetrahedral coordination for the metal ions involved. It can be assumed that the oxide ions will provide a moderately weak crytal field. Data obtained for the cobalt-chrome pigment with a mode particle size of 0.8 μ m, show five absorption bands found at 416, 630, 650, 1260 and 1400 nm which corresponds to electronic transitions in tetrahedral Co^{2+} and octahedral Cr^{3+}. The strong absorption band is observed at 630 nm and the corresponding color of this pigment is bluish green (13). Data obtained for the cobalt-manganese pigment show four absorption bands at 580, 700, 1400 and 1800 nm, the most intense being the band at 580 nm. The color of this pigment is dark blue, owing to the absorption of octahedral Mn^{3+} ions. These spectra are characterized by a strong band region between 580 and 630 nm.

In general, tetrahedral complex have more intense absorption than octahedral complex. This is a consequence of the first selection rule: transitions between d orbitals in a complex having a center of symmetry are forbidden. As a result, absorption bands for octahedral complex are weak in tetrahedral complex, the lack of a center of symmetry makes transitions between d orbitals more allowed. The cobalt ion in these pigments is located in a tetrahedral site. As might be inferred from the simple observation that octahedral complexes are typically pale red or purple, many common tetrahedral ones are typically pale red or purle, many common tetrahedral ones are an intense blue. In each case the visible spectrum is dominated by the highest energy transition, and the blue color in these pigments may be attributed to this transition:

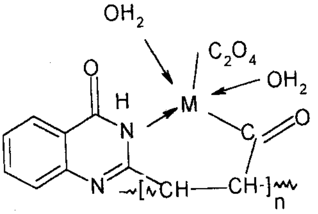
$$^4A_2 \longrightarrow {}^4T_{1(P)}$$

According to the crystal-field model, the energy level of the 3d electrons in a transition metal ion placed in a tetrahedral environment splits into a lower doublet e_g and a higher triplet t_{2g}. Thus, four of the seven d electrons of the Co^{2+} ion occupy the e_g orbital and the remaining three occupy the t_{2g} orbital in the ground state. The visible transitions in the tetrahedral site, generally have complex. Envelopes decaute a number of transitions to doublet excited states occur in the same region, and these acquire some intensity by means of spin-orbit coupling(16).

The color became bluish green in the case of $CoCr_2O_4$ and dark blue in $CoMn_2O_4$ by the overlapping of Co^{2+} absorption bands with Cr^{3+} absorption bands, and Co^{2+} with Mn^{3+} respectively.

Figure 3(a) shows a micrograph for a $CoCr_2O_4$ precursor powder heat-treated at 550 °C, and Figure (b) at 700 °C. At 500 °C the spinel phase starts to crystallize and at 600 °C the phase is totally formed. The mean particle size ranges from 0.8 to 0.9 μm. This pigment displays a grain morphology consisting of perfect octahedrons characteristic of spinels.

Finally, the halogen complexes are most stable. It is evident that differences in the initial decomposition temperature of step 2 for the polymer complexes are due to the influence of the anion. The dehydration energy calculated for these effects varied between 40.0 and 29.0 kJ mol^{-1} while ΔH=52.0 kJ mol^{-1} (per H_2O released) for compound of nature complex (14).



where M=Cr^{3+} and Co^{2+}

The synthesis of thermally stable polychelates and their thermal decomposition now promises an interesting area in the chemistry of heat-resestant polymers. Some of the polymers containing metal ion linked by chelate rings derived from organic backbone units are much.

Table 2. Activation energies for the thermal degradation of polymer complexes

Species[a]	**E_a (KJ mol^{-1})**
1-$CoAl_2O_4$	29.3
2-$CoCr_2O_4$	35.0
3-$CoMn_2O_4$	40.0
4-N-Arolylquinazoline	12.4

More stable than aliphatic rings, and have significantly higher melting temperatures according to my previous work(14). The greater stabilities of the polymer complexes compared with homopolymer may be due to the formation of six-membered ring structures in the homopolymer complexes. The values of energy of activation (E_a) (Table 2) for dehydration of the polymer complexes were determined from TG and DTA curves.

Conclusion

$CoAl_2O_4$, $CoMn_2O_4$ and $CoCr_2O_4$ spinel pigments were synthesized from a mixed solution of metal chlorides in the presence of aqueous ammonia under hydrothermal conditions, confirmed that all three pigments revealed the formation of single spinel, with particle size of 1.2, 2.1 and 0.8 μm, respectively. In these systems, x=0. They are normal spinels, blue color developed , giving deep absorption characteristic of tetrahedral Co^{2+} ions at about 550-680 nm. However, with substitution of Al^{3+}, Cr^{3+} and Mn^{3+}, the color changes the king's blue with Al^{3+}, to bluish green with Cr^{3+} and dark blue with Mn^{3+}.

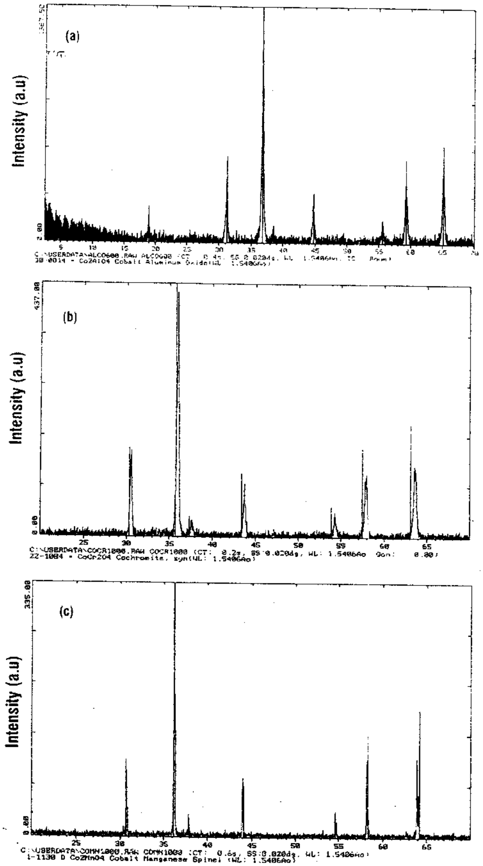


Fig. 1. X-ray diffraction pattern of the Pigments
a)$CoAl_2O_4$ b)$CoCr_2O_4$ c)$CoMn_2O_4$

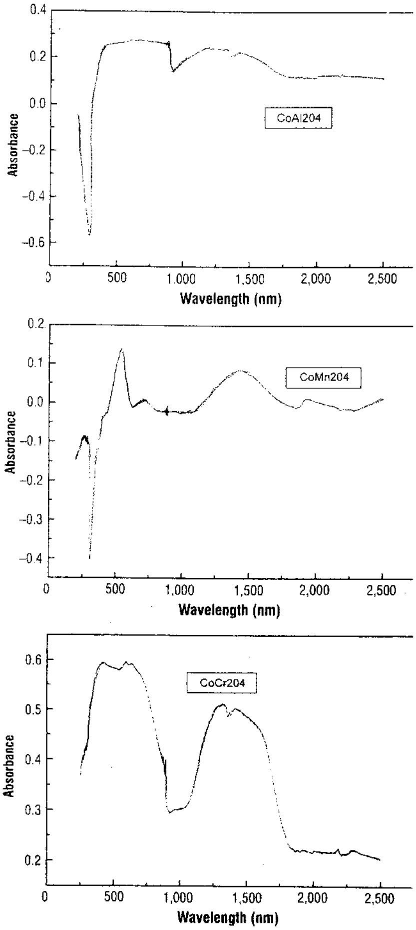


Fig.2. Diffuse reflectance of
a)$CoAl_2O_4$ b)$CoCr_2O_4$ c)$CoMn_2O_4$

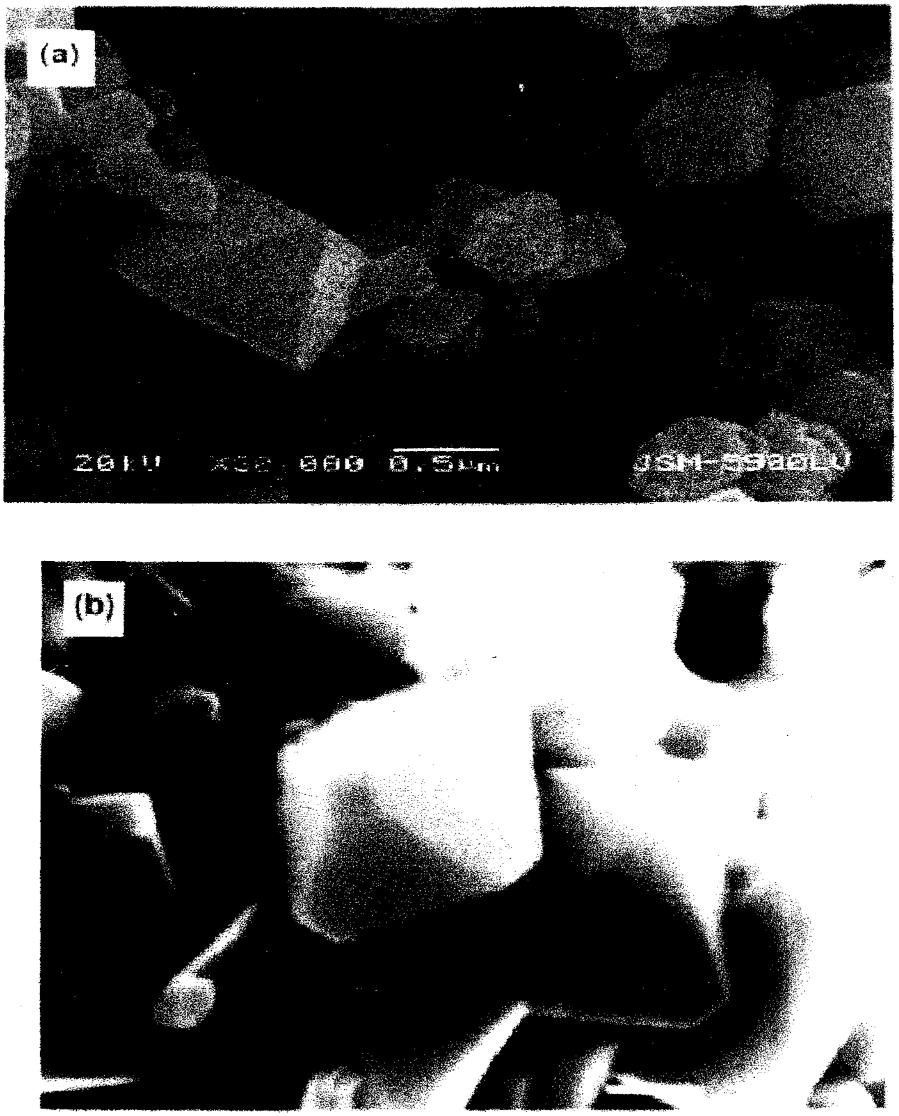


Fig.3. SEM micrographs of the $CoCr_2O_4$ Synthesize at (a) 550 °C (b) 700 °C

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