

Synthesis of CoAl_2O_4 spinel from cobalt-loaded zeolite-A

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Abstract: - One of the methods for synthesis of CoAl_2O_4 is calcination of cobalt loaded zeolite which is yielded via ion-exchange treatment on zeolites. In the present work for the first time the phase evolution of cobalt loaded zeolite-A studied by simultaneous thermal analysis. To get better understanding of microstructure of products x-ray diffraction and scanning electron microscopy were taken. Results showed that zeolite collapse and spinel nucleation happen around 845°C, in which nanocrystalline spinel are being dispersed within the amorphous siliceous matrix.

Keywords: - cobalt aluminate, spinel, zeolite A, ion-exchange, pigment

I. INTRODUCTION

Cobalt aluminate normal spinel (CoAl_2O_4) is known as an idiochromatic ceramic blue pigment whose blue color is attributed to tetrahedrally coordinated Co^{2+} ions [1,2]. As cobalt aluminate spinel possesses basicity and redox capability and is stable at high temperatures, potential application of the composition has been studied for heterogeneous catalyst in reforming of methane, capture and decomposition of nitrous oxide and capture of carbon dioxide [3]. Then to take full advantage of the mixture for those applications, so far four synthesis approaches have been reported. Among the methods, solid state reaction between the corresponding metal salts like oxides and carbonates powders through conventional heating is considered as a reliable and common method for synthesis of the spinel. But this method has some drawbacks: a) seeks heating at high temperatures, above 1200°C, b) is time consuming, at least 10 hours, c) inevitable inhomogeneity of the mixed powders, thereby, existing some unwanted compounds after calcination like: Al_2O_3 , Co_3O_4 , CoO and spinel with $\text{Co}/\text{Al} \geq 0.5$ ($\text{Co}^{2+}\text{Co}_x^{3+}\text{Al}_{2-x}\text{O}_4$) at which the extra cobalt ions as Co^{3+} would be placed in octahedral positions and bring green to black tint into the pigment [1,2,4,5]. Some alternative methods such as sol-gel [5-8], co-precipitation [9] and cobalt-loaded zeolite [4,10,11] have been suggested in recent years in order to get rid of different problems in solid state reaction.

Cobalt-loaded zeolite method consists of two steps, ion-exchange and calcination. In ion exchange treatment, the extra framework cations of zeolite (here Na^+ for zeolite A) are replaced by Co^{2+} and the product is called "cobalt-loaded zeolite" or "cobalt-exchanged zeolite". Heating the cobalt-loaded zeolite collapses zeolite framework and cobalt aluminate spinel nucleates simultaneously in an amorphous matrix. This amorphous matrix brings some advantages, including: a) a better and sooner matching of pigment particles with glaze and also delaying the dissolution of pigments in glaze, b) to limit the escape of harmful cobalt ion into the environment, c) to prevent spinel crystals from being agglomerate during calcination. Leaching away the matrix gives well separated fine spinel crystals that are appropriate for catalyst application. Moreover, some general advantages of the route are summarized in the following: a) ion-exchange treatment gives a uniform elemental

distribution of Co^{2+} ions in the atomic scale beside Al^{3+} ions in zeolite framework. Then atomic diffusion, which is as a main barrier in solid reaction process, would be largely promoted [4,5,10], b) in maximum rate of ion-exchange each of the two Al^{3+} ions are balanced by one Co^{2+} . Then, the molar ratio of Co/Al would be equal or less than 0.5. Therefore, there would be no need to be concerned about the formation of cobalt aluminate spinels with $\text{Co/Al} \geq 0.5$ ($\text{Co}^{2+}\text{Co}_x^{3+}\text{Al}_{2-x}\text{O}_4$). This method also has some advantages in comparison with co-precipitation and sol-gel. Co-precipitation often gives non-uniform product in large batches. Moreover, the alumina which is often formed from inhomogeneous precursors cannot be dissolved as easy as silica. Alkoxide precursors for sol-gel method are expensive and strict safety precautions have to be observed during the calcination step.

Chemically, zeolites are represented by the empirical formula $\{\text{M}_{2/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2 \cdot w\text{H}_2\text{O}\}$ where M is extra-framework cation belongs to groups IA or group IIA elements, such as sodium, potassium, magnesium and calcium. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by extra-framework cation. The cations are mobile and ordinarily undergo ion exchange [12]. Cation exchange capacity (CEC) of zeolites is depended on some factors like: 1) size of channel's window of zeolite's structure, 2) Si/Al molar ratio in zeolite formula. Low silica zeolites ($1 \leq \text{Si/Al} \leq 1.5$) like zeolite-A which is chosen for following experiments have higher CEC in comparison with high silica zeolites [13]. 3) charge density (charge/size) of ion that is supposed to enter into the zeolite as a guest ion, 4) size of guest ion and hydrated guest ion [13,14], 5) hydration energy of guest ion [14-16], 6) pH [14,17-19], 7) electrostatic bonding energy of the competing ions to the inner cavity surface of zeolite, [14]. 8) temperature [15-18,20,21]. Although several works has been conducted to determine cobalt-loaded zeolite-A properties [4,10,11], still there is no exact insight about thermal behavior of ones. The motivation of the existing research is to investigate and implement thermal behavior of the pigment and subsequently phase evolution. For this means, STA and XRD equipments was utilized to explain the changes during heating process.

II. MATERIALS AND METHODS

Ion exchange was done at 85°C for 30 minutes in agitating aqueous solution of cobalt chloride with concentration of 0.1 M and solid/solution weight ratio of 30 g/lit. The purity of zeolite-A powder and hydrated cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was 90% and 98%, respectively. The pH of suspension without adding additive was 6 and didn't change. Fig. 1 shows the steps followed in this investigation for synthesis of cobalt aluminate normal spinel via "cobalt-loaded zeolite" method. Cobalt-loaded zeolite-A that yielded from ion exchange treatment was filtered, washed with deionized water, dried and then calcined.

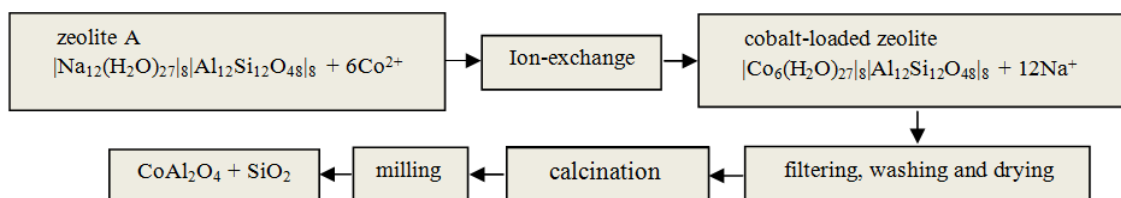


Figure 1: Steps involved in synthesis of CoAl_2O_4 from zeolite-A via "cobalt-loaded zeolite" method.

Calcination was done in two separate groups for different aims.

First group of calcinations

In order to find out what phase evolutions happen at peak temperatures detected by differential thermal analysis (DTA). First of all prepared samples heated up to the given temperatures taken by that thermal analysis tool with same heating rate as the DTA analysis ($10^\circ\text{C}/\text{min}$). just after hitting the determined temperatures samples quenched in front of blowing cold air (5°C).

Second group of calcinations

Samples held at determined temperatures (ranging from 600 to 1200°C) for 5 hours for the sake of accomplishment of the spinel crystal growth and then cooled down within the furnace to room temperature. The characterizing tools used in this research: X-ray diffraction (XRD) in a Philips Expert diffractometer with Ni filtered $\text{CuK}\alpha$ radiation. Energy dispersive X-ray (EDX) with VEGA\\TESCAN microscope operated in voltage 30 kV. High resolution transmission electron microscopy (HRTEM), model: Tecnai TF20 FEGTEM, operating at 200 kV. Simultaneous thermal analysis (STA) was done with a NETZSCH STA 409 PC/PG instrument with heating rate of ($10^\circ\text{C}/\text{min}$).

III. RESULTS AND DISCUSSION

As shown in Fig.1 first step is ion-exchange treatment in which two Na^+ ions in zeolite-A structure are replaced by one Co^{2+} ion. Fig. 2 shows the map of Co^{2+} ion in cobalt-loaded zeolite-A (Fig. 2.c), and map of Na^+ ion for both zeolite-A and cobalt-loaded zeolite-A, (Fig. 2.b and d, respectively). Fig.2 further reveals a uniform distribution of Co^{2+} was formed in zeolite powder after the ion-exchange treatment, thereby reducing the population of Na^+ ions. Size of channel's window of zeolite-A is $(4.1 \times 4.1 \text{ \AA})$ [22] meanwhile the size of cobalt ion (Co^{2+}) is estimated around 1.3\AA and for completely hydrated cobalt $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is approximately 8.46\AA in diameter [13]. In this situation some of the H_2O molecules around the hydrated cobalt ion are stripped of to allow successful passage of the narrow windows [14].

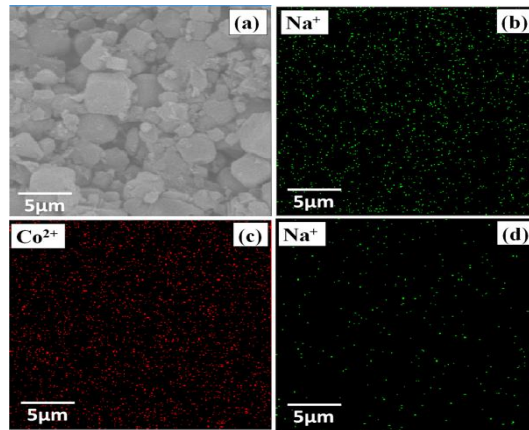


Figure 2: SEM micrograph of zeolite-A powder (a), map of Na^+ ion in zeolite-A (b), map of Co^{2+} and Na^+ ions in cobalt-loaded zeolite-A (c and d, respectively).

STA analysis of cobalt-loaded zeolite-A is given in Fig. 3. According to the TGA graph, 27% weight loss happens by 600°C . The reduction in weight is attributed to crystalline water and superficial water and also would be much legal when the weight loss number is being compared with weight loss one (24%) that is indicated in case of zeolite-A formula. In order for distinguishing slight weight changes as much as, derivation TG graph (DTG) in terms of time was taken (see Fig.4). The two distinct peaks shown in DTG which are assigned at 120 and 175°C (Fig. 4) are matched with an obvious endothermic peak at 120°C and a slight slope change about 175°C in DTA graph (Fig.3) respectively. Generally, there are two types of H_2O molecules in channels of zeolites structural: (a) H_2O molecules coordinating the extra-framework cations and (b) "spacefilling H_2O molecules" bonded by hydrogen bonds to the cavity surface. While hydrated zeolite is being heated, the released H_2O first is bonded to extra-framework Na, and followed deal mainly by "spacefilling" hydrogen-bonded molecules [14]. Accordingly, the endothermic peak and weight loss at 120°C might mostly be related to exiting the H_2O coordinating extraframework Na and the "spacefilling" H_2O molecules release is expedited around 175°C .

Oxidation of Co(II) to Co(III) happens about 300°C [2] then the weak exothermic broad peak around 310°C in DTA graph (Fig. 3) can be related to this oxidation although there is not a clear sign of oxygen absorption and consequent weight increase in the TG and DTG graphs (Fig. 3 and Fig. 4). Dropping the DTA graph after 1050°C (Fig. 3) can be the result of melting the glass matrix.

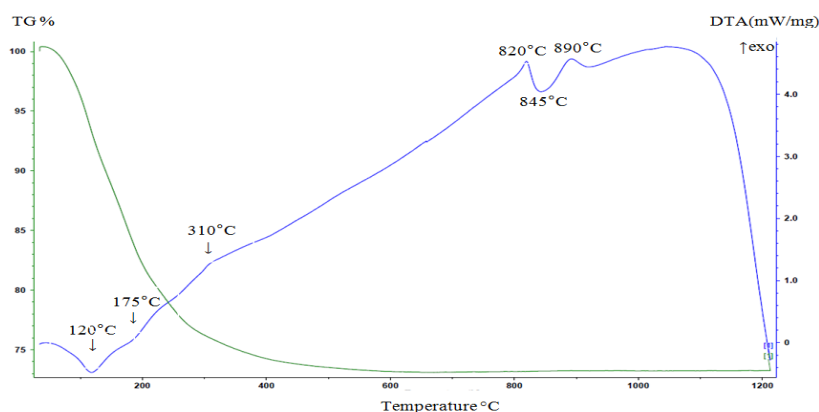


Figure 3: STA analysis of cobalt-loaded zeolite-A.

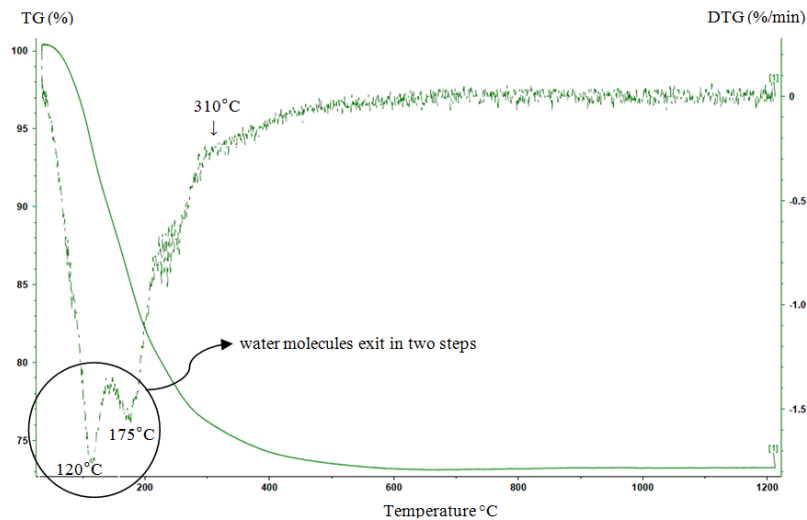


Figure 4: TG and DTG graphs which are obtained from STA analysis of cobalt-loaded zeolite-A.

Three more peaks can be distinguished in the DTA graph: two exothermic at 820 and 890°C and one endothermic at 845°C. In order to find out what phase evolutions happen at these temperatures the *first group of calcinations* was performed. The XRD phase analysis of products are shown in Fig. 5. As this figure shows all the peaks in XRD pattern of samples-820°C belong to zeolite-A which means that zeolite structure is remained stable until this temperature. Conclusively, the supposed weak exothermic peak at 820°C in DTA graph (Fig. 3) should not be taken a signified peak because no phase evolution happens at this temperature. The XRD pattern of sample-845°C shows that at this temperature zeolite framework collapses which results in appearing an endothermic peak at this temperature in DTA graph (Fig. 3). Moreover, a broad peak at $2\theta=65.5^\circ$ can be distinguished in this pattern which belongs to cobalt aluminate spinel and is the sign of spinel nucleation in parallel with zeolite collapse. Perhaps the exothermic effect of crystal nucleation about 845°C is dominated by the endothermic effect zeolite collapse.

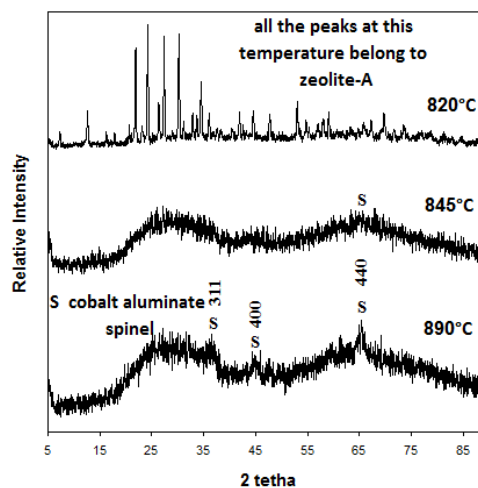


Figure 5: XRD phase analysis of *first group of calcinations* products. Samples are heated until 820°C, 845°C and 890°C and quenched in front of blowing cold air.

In the XRD pattern of sample-890°C three peaks belong to cobalt aluminate spinel appears. The exothermic peak at 890°C in DTA graph (Fig. 3) can be related to the vast nucleation and growth of cobalt aluminate spinel. The collapse of zeolite framework is necessary for the nucleation of spinel. In fact, these two occur simultaneously. The temperature of this transition depends on type of zeolite and guest transition element [10]. This temperature is reported between 750°C-770°C by M.T.J. Lodge et al [4], who used zeolite-X as precursor and 840°C by W. Schmidt et al [10] who used ambient pressure for calcination of cobalt-loaded zeolite-A.

In order to complete the spinel crystal growth *second group of calcinations* was performed. Fig. 6. shows the XRD phase analysis of products. The XRD results show that the zeolite structure is until 600°C. At 800°C zeolite framework collapses and distinct peaks belonging to cobalt aluminate spinel structure appear.

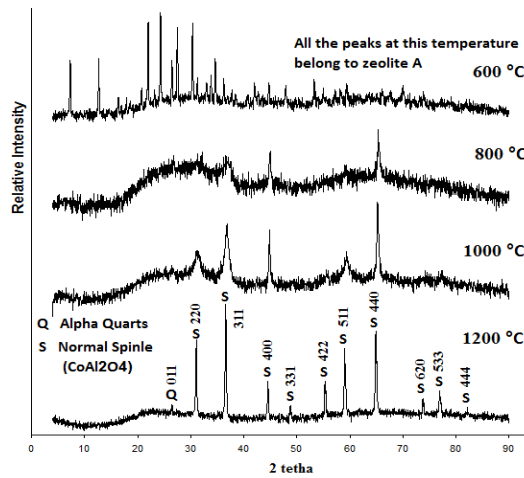


Figure 6: XRD phase analysis of *second group of calcinations* products. Samples are heated at 600, 800, 1000 and 1200°C for five hours and cooled down within the furnace.

Comparing the XRD patterns of sample-800°C in Fig. 6. and sample-890°C in Fig. 5. it can be concluded that holding the sample at calcination temperature for 5 hours has helped zeolite structure collapsing and spinel nucleation and decreases the temperature of this transition more than 100°C. Fig. 6. further reveals that with increasing the heating temperature to 1000 and 1200°C the spinel structure peaks become narrower and more intensified. The weak peak at $2\theta=26.4^\circ$ which can be distinguished in XRD pattern of sample-1200°C is for alpha quartz structure and all the other peaks belong to normal spinel (CoAl_2O_4). The peak at $2\theta=48.1^\circ$ confirms that the yielded spinel is "normal" spinel [2]. Moreover, the broad hill in the range $20^\circ < 2\theta < 30^\circ$ is related to the amorphous phase consist of Si remained from collapsing the zeolite-A plus oxygen, sodium and probably some unreacted aluminum.

HRTEM image of sample 1200°C is given in Fig. 7.a. The image reveals cubic crystals and polycrystals of CoAl_2O_4 embedded in an amorphous matrix. Fig. 7.b shows the TEM diffraction pattern of one of these crystalline areas. In Fig. 7.b the distance between diffraction points and center is equal to $1/d = R/(\lambda \cdot L)$ which d is lattice space, R is vector distance, λ is wavelength and L is camera length. Other than two diffraction points, (310) and (330), which belong to alpha quartz, Other ones are assigned for spinel structure. Some of the diffraction points which belong to one zone-axis are indexed.

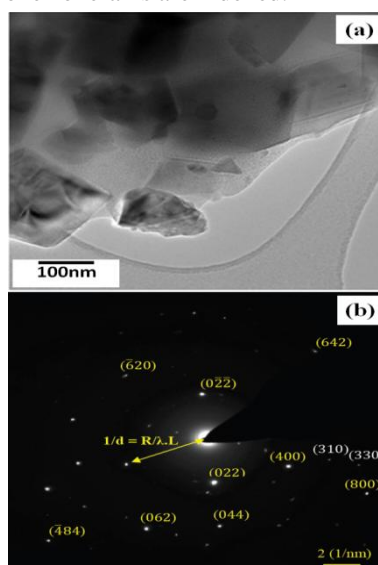


Fig. 7. HRTEM images of sample 1200°C which shows spinel's cubs embedded in amorphous matrix (a), TEM diffraction pattern of one of these crystalline areas (b).

The average crystallite size of CoAl_2O_4 was calculated using Sherrer formula, below, [23] for samples synthesized at 1000 and 1200°C (Table 1).

$$t = \frac{0.9\lambda}{B \cos\theta_B}$$

Where t is particle diameter, λ is the wavelength of the incident X-ray radiation, θ_B is the Bragg angle that exactly satisfies the Bragg law and B is the width at half maximum height of the analyzed reflection. The results in Table 1 show that increasing the temperature from 1000 to 1200°C causes a substantial crystal growth from 12 to 43.3 nm in average. The average size of crystals in TEM images (Fig. 7) seems bigger than what was calculated via Sherrer formula through XRD patterns (Table 1). A part of this disagreement could be because of the fact that the crystals observed in TEM image can be polycrystalline and the Deby Sherrer formula only gives the average crystallite size.

Table 1. The average crystallite size of CoAl_2O_4 calculated from Deby Sherrer formula for samples calcined at 1000 and 1200°C

Temp	Average crystallite size
1000°C	12 nm
1200°C	43.3 nm

IV. CONCLUSION

Using ion-exchange treatment, Co^{2+} ions uniformly disperse into the zeolite-A structure. By heating the "cobalt-loaded zeolite-A" the two special types of H_2O molecules, spacefilling and H_2O coordinating the extra-framework cations, go out mostly at 175 and 120°C respectively. Collapse of zeolite structure and nucleation of spinel happen simultaneously around 845°C. Blue cobalt aluminate normal spinel crystals dispersed in a silicious matrix is the final product of calcination process. The average crystallite size for sample calcined at highest temperature (1200°C) for 5 hours was 43.3 nm.

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