Scientific Research Publishing

Open Journal of Synthesis Theory and Applications, 2017, 6, 13-22
http://www.scirp.org/journal/ojsta
ISSN Online: 2168-1252
ISSN Print: 2168-1244

Synthesis of Cu-Chromite Catalyzer by Citrate Sol-Gel

Pouresmaeily Seyed Mohammad[1*], Shahidzadeh Mansour[1], H. Shirkavand Behzad[2], Ebrahimi Sobhan[3]

[1]Department of Chemistry &Chemical Engineering, Malek-e-Ashtar University of Technology, Tehran, Iran
[2]Institute for Color Science & Technology, Tehran, Iran
[3]Department of Material Science and Engineering, Sharif University of Technology, Tehran, Iran
Email: *smpouresmaeily@hotmail.com

How to cite this paper: Mohammad, P.S., Mansour, S., Behzad, H.S. and Sobhan, E. (2017) Synthesis of Cu-Chromite Catalyzer by Citrate Sol-Gel. *Open Journal of Synthesis Theory and Applications*, **6**, 13-22.
https://doi.org/10.4236/ojsta.2017.62002

Received: April 1, 2017
Accepted: April 27, 2017
Published: April 30, 2017

Abstract

It has been introduced several ways for rising fuel burning rate. Using catalyzers is a common way to rising fuel burning rate. Cu-Chromite catalyzer used in solid fuels, as burning rate catalyzer in thermal decomposition of Ammonium Perchlorate and results were satisfying. This catalyzer is produced by several methods such as: ceramic, coprecipitating, sol-gel, vacuum depositioning, but this paper explains producing catalyzer by Citrate sol-gel. Thermal analysis is used for studying process also SEM, XRD, TEM, FTIR tests used for determination of particle sizes.

Keywords

Nano Cu-Chromite, Citrate Sol-Gel, Catalyzer, Burning Rate, Ceramic Method

1. Introduction

In recent years the Cu-Cr-O composites are found great promising in application as burning rate catalysts (ballistic modifier) for solid propellants used in defense (high explosives, ballistic missiles) and space vehicles (rocket propellants). Solid composite propellants are mixtures of prepolymer (binder), aluminum fuel, oxidizer salts (e.g. ammonium perchlorate), and other components, including curatives, plasticizers, bonding agents, stabilizers and catalysts. Even though added at few percent of the propellant binder, the catalysts used to control the burn rate are of high importance, since they allow improving the ballistics of rockets [1]. Combustion of this system involves the decomposition of AP (ammonium perchlorate) and the binder and mixing and oxidation-reduction of the decomposition products. Rajeev *et al.* prepared Cu-Cr-O composite oxides

via thermal decomposition of copper ammonium chromate and found that the propellant burning rate is enhanced by the addition of Cu-Cr-O composite oxides. Li *et al.* used Cu-Cr-O nanocomposites as additives for the catalytic combustion of AP-based solid-state propellants, synthesized via a citric acid (CA) complexing approach. They showed that well crystallized Cu-Cr-O nanocomposites could be produced after the CA-Cu-Cr precursors are calcined at 500˚C for 3 hrs. Addition of the as synthesized Cu-Cr-O nanocomposites as catalysts enhances the burning rate as well as lowers the pressure exponent of the AP-based solid-state propellants considerably. Noticeably, catalyst with a Cu/Cr molar ratio of 0.7 exhibited promising catalytic activity with high burning rate and low pressure exponent at all pressures, due to the effective phase interaction between the spinel $CuCr_2O_4$ and delafossite $CuCrO_2$ contained in the as-synthesized Cu-Cr-O nanocomposites. Patil, *et al.* synthesized p-type nano-CuO and $CuCr_2O_4$ by an electrochemical method and investigated the catalytic effect on the thermal decomposition behavior of ammonium perchlorate (AP) as a function of catalyst concentration using differential scanning calorimetry. The nano copper chromite ($CuCr_2O_4$) showed catalytic effect as compared to nano-cupric oxide (CuO) in lowering the high temperature decomposition by 118˚C at 2 wt%. They observed high heat released of 5.430 and 3.921 kJ g^{-1} in the presence of nano-CuO and $CuCr_2O_4$, respectively. The decrease in the activation energy and the increase in the rate constant for both the oxides confirmed the enhancement in catalytic activity of AP. They proposed a mechanism based on an electron transfer process for AP in the presence of nanometal oxides.

2. Ceramic Method

The vast majority of the powder synthesis of high temperature superconducting oxides to date has been carried out using the traditional "solid-state reaction route". Copper chromite spinels are usually synthesized by the conventional high temperature method of solid state reaction (Equation (1)): [2]

$$CuO_{(s)} + Cr_2O_3 \xrightarrow{6hrs,900^{\circ}C} CuCr_2O_4 \quad (1)$$

Kawamoto *et al.* prepared copper chromite by ceramic method, mixing copper (II) and chromium (III) oxides at 3 different ratios Cu/Cr = 0.61; Cu/Cr = 1.0; Cu/Cr = 1.5. The mixtures of oxides were homogenized with acetone followed by subsequent calcination at 900˚C for 6 hours. This method results in spinel particles with low surface areas. In order to synthesize spinels with high surface area, they attempted different wet chemistry techniques.

3. Materials and Methods

By this method, Cu and Potassium dichromate with Ammoniac and deionized water mixed with specific ratio (determines the particle size of final Chromite) then dried the outcome precipitate in 110˚C and 500˚C for twice finally, Cu-Chromite produces

$$2CuSO_{4(aq)} + K_2Cr_2O_{7(aq)} + 4NH_3 + 3H_2O$$
$$\rightarrow 2Cu(OH)NH_4CrO_{4(s)} + K_2SO_{4(aq)} + (NH_4)_2SO_{4(aq)}$$
$$2Cu(OH)NH_4CrO_{4(s)} \xrightarrow{110\text{-}500^\circ C} CuO_{(s)} + CuCr_2O_{4(s)} + 5H_2O$$

Vacuum precipitating is a laboratory method, that isn't economical because of problems of performing such as: low temperature, high vacuum for producing catalyzer. By studying different factors: ease of perform, low costs, uniform particle size, Citrate sol-gel was choice for producing catalyzer.

3.1. Catalyzer Fabrication

Li *et al.* have prepared Cu-Cr-O nanocomposites by citric acid (CA) complexing approach in which 0.01 mol $Cu(NO_3)_2$ and 0.02 mol $Cr(NO_3)_3$ are dissolved in 100 mL deionized water to obtain a mixed metal nitrate solution. Then citric acid is added to this solution and the molar ratio of citric acid to the total metal ions is fixed to be 2:1. After stirring for 30 min, the solution is heated at 95˚C for several hours to evaporate the water solvent to produce dark brown transparent viscous gels. The gels are then dried at 160˚C for 2 hrs to obtain the foamy dark powders, which are denoted as precursors of Cu-Cr-O nanocomposites (CA-Cu-Cr). After grinding, the precursors are successively heated at 600˚C for 3 h to obtain the final black Cu-Cr-O nanocomposites [3].

3.2. Characterization Methods

Thermal decomposition process acts with thermal analysis of DTA/TG model SAT1649 device with heating rate 10˚C/min in air. Solid phases detects with XRD device, model Xpert-Philips with CuKα radiations. Outcome Chromite nano particles calcinated sizes measures with SEM images of Philips-Xl30 model device.

4. Results and Discussion

4.1. Citrate Self-Burning Behavior

Results shows that produced Citrate gel from metal Nitrates and Citric acid goes through self-burning. By heating, bright points appear. This process studied by thermal analysis. **Figure 1** shows that in DTA diagram, exothermic reaction acts in 237˚C. This reaction is because of reduction-oxidation reactions between Citrate system and Nitrate [4]. Diagram TG also shows that decomposition of gel occurs suddenly and randomly. In this temperature (237˚C) gel begins to burn. Weight loss of gel is about 80% that occurs with self-burning. This weight loss is because of removing water vapor, carbon dioxide and nitrogen oxide.

4.2. Phase Analysis and Particle Size Determination

Figure 2 shows that ash produces as result of drying in 160˚C then calcination in

[1]Differential thermal analysis and Thermo gravimetric
[2]X-ray Diffraction
[3]Scanning Electron Microscope

600˚C, includes different oxides of Cu and Cr compounds in Figure 2, also Figure 3 shows nano particle sizes which measured with SEM.

4.3. FT-IR Spectrum

FT-IR spectrum of produced particles shows some peaks in 524 cm^{-1}, 563 cm^{-1} and 611 cm^{-1}, represents bending vibrations of Chromite anion ($Cr_2O_4^-$) in solid phase ($CuO{\cdot}CuCr_2O_4$) (Figure 4). The peak of 1637 cm^{-1} is for CuO vibrations. Existing solid phase ($CuO{\cdot}CuCr_2O_4$) can proved by spectrum data [5]. Reported

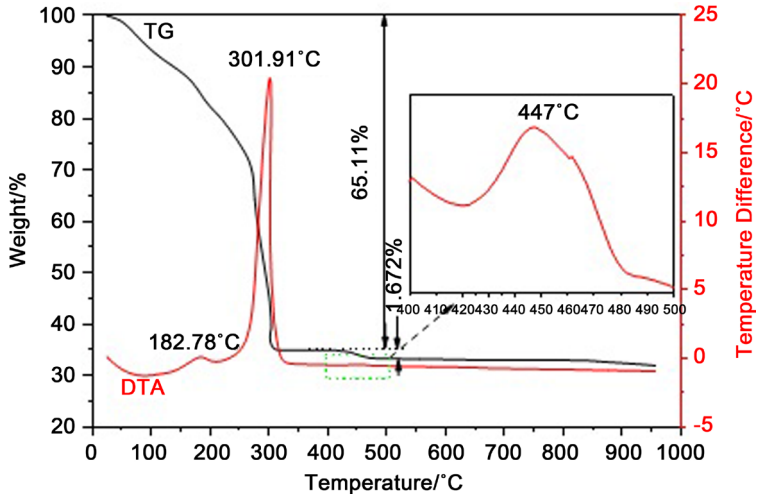


Figure 1. Thermal analysis diagram.

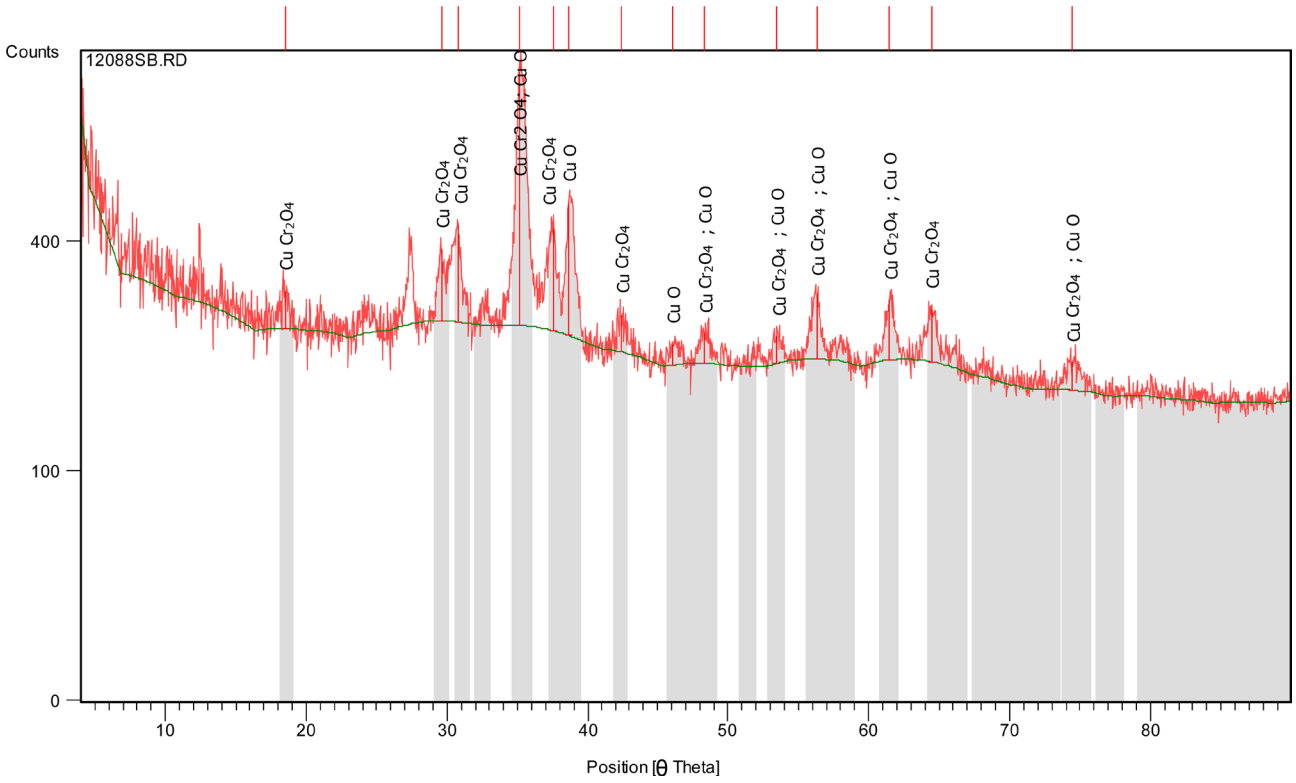


Figure 2. XRD results.

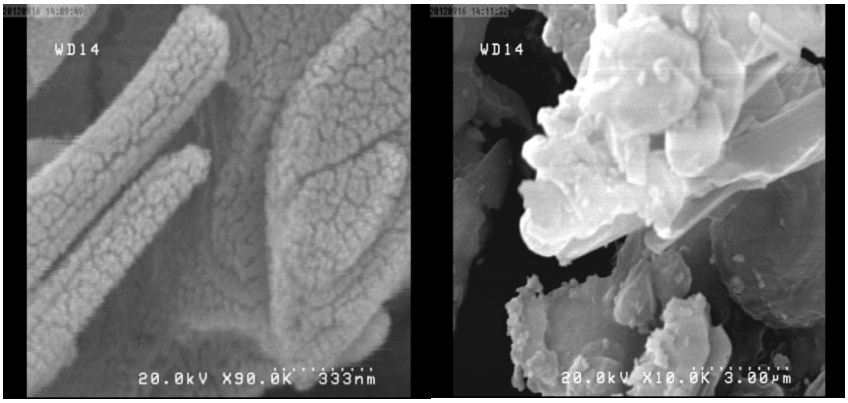


Figure 3. SEM images.

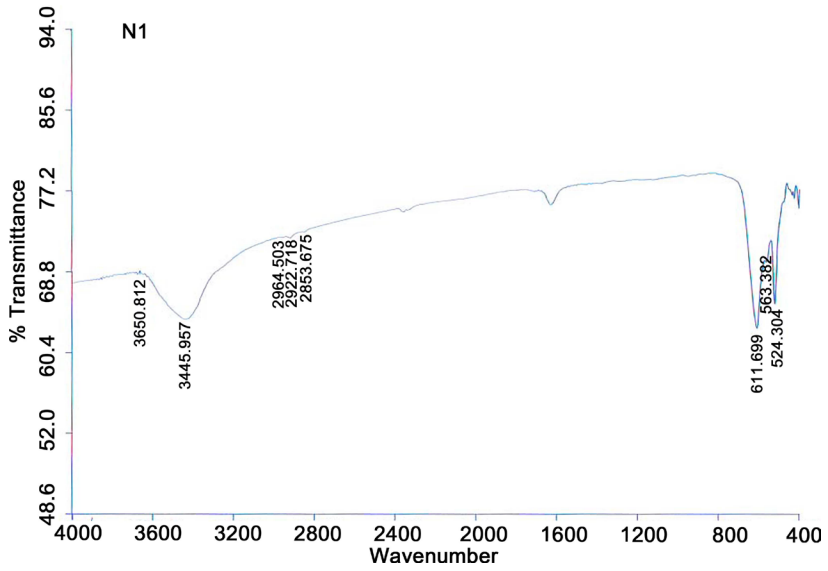


Figure 4. Ft-Ir test results for produced particles.

studies compatibility the empirical data with FT-IR spectrums by Miller and Willkins for mineral onions.

4.4. Measuring Produced Particles Size

In polycrystalline materials, width of peak of XRD increases with decreasing crystalline plane spacing. The most useful pattern for measuring grain size, is use the FWHM[4] formula that shown in **Figure 5**. FWHM, depends on the number of reflecting crystalline plane. Scherer formula relates the crystalline grain size to width of maximum peak in half height and other conditions [6].

Table 1 shows the FWHM details. By substituting values in formula of FWHM, the mean particle size is 47 nm.

4.5. Measuring and Determining Synthesized Productions Crystalline Type by TEM Images

Figure 6 shows that synthesized particles size is 50 nm that confirms diffraction

[4]Full width at half maximum.

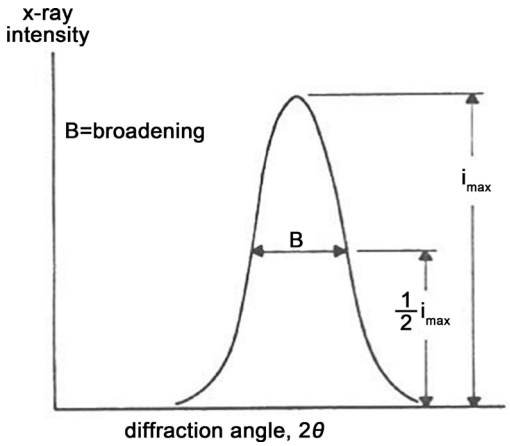


Figure 5. FWHM method.

Table 1. FWHM values.

Pos. [˚2 Th.]	Height [cts]	FWHM [˚2 Th.]	d-spacing	Rel. Int. [%]	Tip width [˚2 Th.]	Matched by
18.4897	55.39	0.4723	4.79874	11.48	0.4800	01-072-1212
29.5914	111.12	0.3936	3.01887	23.04	0.4000	01-072-1212
30.7835	155.31	0.4723	2.90462	32.20	0.4800	01-072-1212
35.1639	482.28	0.2755	2.55218	100.00	0.2800	01-072-1212
37.5089	162.56	0.3936	2.39784	33.71	0.4000	01-072-1212
38.6402	215.94	0.2362	2.33020	44.78	0.2400	01-080-1917
42.3909	50.25	0.6298	2.13231	10.42	0.6400	01-072-1212
46.0739	26.27	0.9446	1.97007	5.45	0.9600	01-080-1917
48.3479	39.30	0.7872	1.88259	8.15	0.8000	01-072-1212
53.4776	35.78	0.6298	1.71348	7.42	0.6400	01-072-1212
56.3144	90.43	0.3936	1.63371	18.75	0.4000	01-072-1212
61.4957	82.90	0.4723	1.50791	17.19	0.4800	01-072-1212
64.4867	72.49	0.6298	1.44501	15.03	0.6400	01-072-1212
74.4494	33.89	1.1520	1.27334	7.03	0.9600	01-072-1212

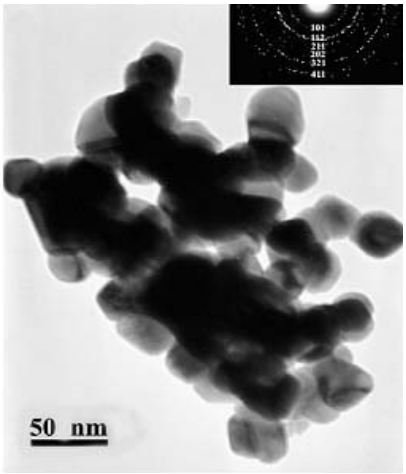


Figure 6. TEM images of synthesized nano catalyzer sample.

data that synthesized production by Citrate sol-gel method in PH of 9, has spinel crystalline that is In accordance with the detected structure in XRD. Synthesized Cu-Chromite in PH of 9 is solid phase of CuO, $CuCr_2O_4$ that has spinel crystalline structure.

4.6. Synthesis of Cu-Chromite Nano Catalyzer in Different PHs

For studying PH effect in synthesis process of Cu-Chromite nano catalyzer, all of last studied method include metal percentage, amount of used Citric acid and drying and calcinating method (environmental conditions) are used and Ammonium solution of 0.1 molar used for controlling PH values. In this step, values of PH set to 3.32 (that is equal to PH of sample without adding Ammonium solution), 5, 7 and 9. Table 2 shows the synthesized samples.

Effect of PH is because of formation of complex of metals and Citrate ion. Actually Citrate ion produces metal citrate complex in solution with free hydrolyzed metals. Synthesizing complex cause of sol to gel transferring. Synthesis this complex is strongly dependent of PH value that can observe by changing the color of synthesized complex in different PH values. For example, the color of complex in PH of 5 is black and is brown for PH of 7. Changing color is because of difference of synthesized Citrate complex [7]. Type of synthesized complex, stable ability amount and thermal decomposition method are effective in phase of solid produced. In different PHs, a synthesis different metal complex that leads to different solid phases by later steps of drying and calcination that by reducing water and other materials. The mean of crystalline dimensions of Cu-Chromite powder calculated by Debby-Scherer relation in PH of 9 is about 85 nm. Results shows that by determining a specific PH could specify the desired type of solid-phase catalysts (Figure 7).

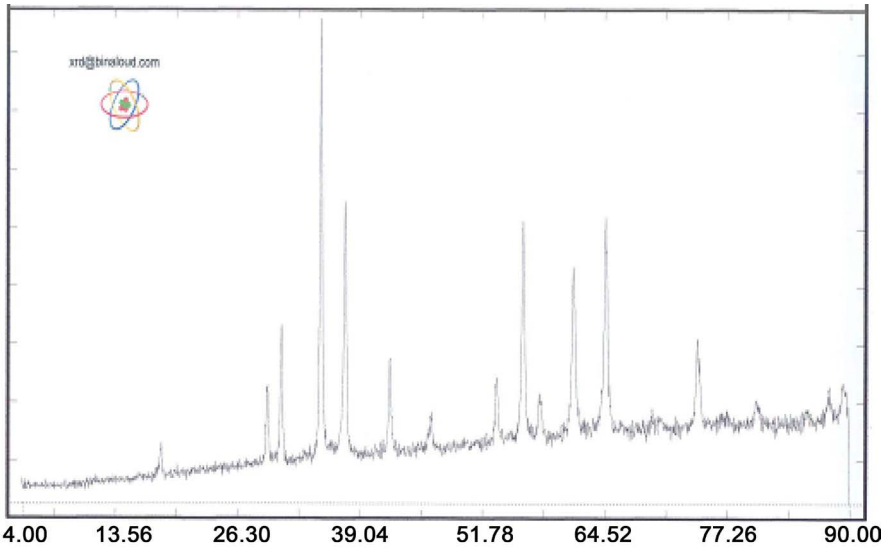
Cu-Chromite that used in increasing fuels burning rate has solid phase of $CuO.CuCr_2O_4$ that synthesis in PH of 9 according to XRD results.

5. Innovation in Catalyzer Synthesis

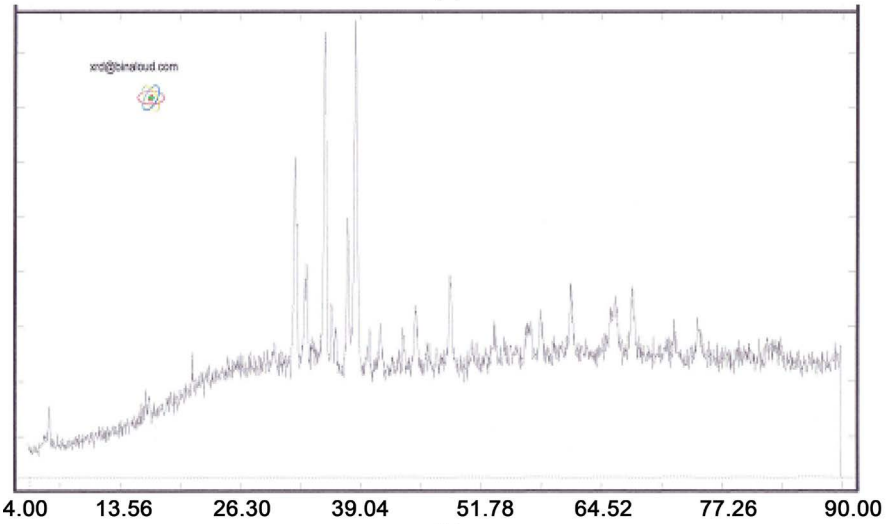
Synthesis Cu-Chromite catalyzer with desired solid phase $CuO.CuCr_2O_4$ leads the researchers attention to synthesis of selected phases of this catalyzer. This phases could synthesized In all of discussed methods. Mentioned phases in Table 2 represent the main consisting phase of particles. Last researches in sol-gel Citrate were based on studying calcination temperature and metals ratio for

Table 2. Cu-Chromite synthesized samples in different PHs.

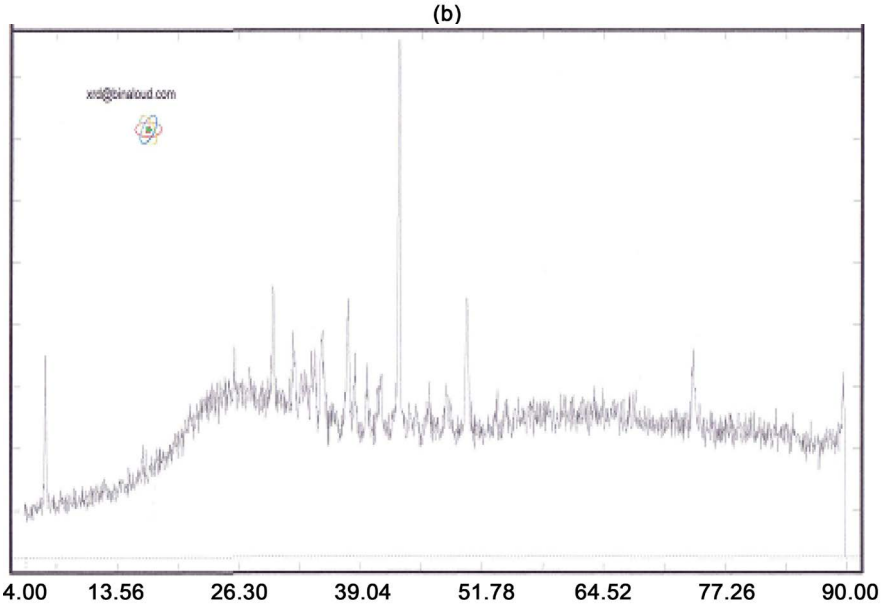
Sample No.	Cu-Cr ratio	Citric acid to total metals molar ratio	Drying	Calcination	PH value
1	0.05	2:1	2 hrs in 160˚C	3 hrs in 700˚C	3.32
2	0.05	2:1	2 hrs in 160˚C	3 hrs in 700˚C	5
3	0.05	2:1	2 hrs in 160˚C	3 hrs in 700˚C	7
4	0.05	2:1	2 hrs in 160˚C	3 hrs in 700˚C	9


4.00
13.56
26.30
39.04
51.78
64.52
77.26
90.00

(a)


4.00
13.56
26.30
39.04
51.78
64.52
77.26
90.00

(b)


4.00
13.56
26.30
39.04
51.78
64.52
77.26
90.00

(c)

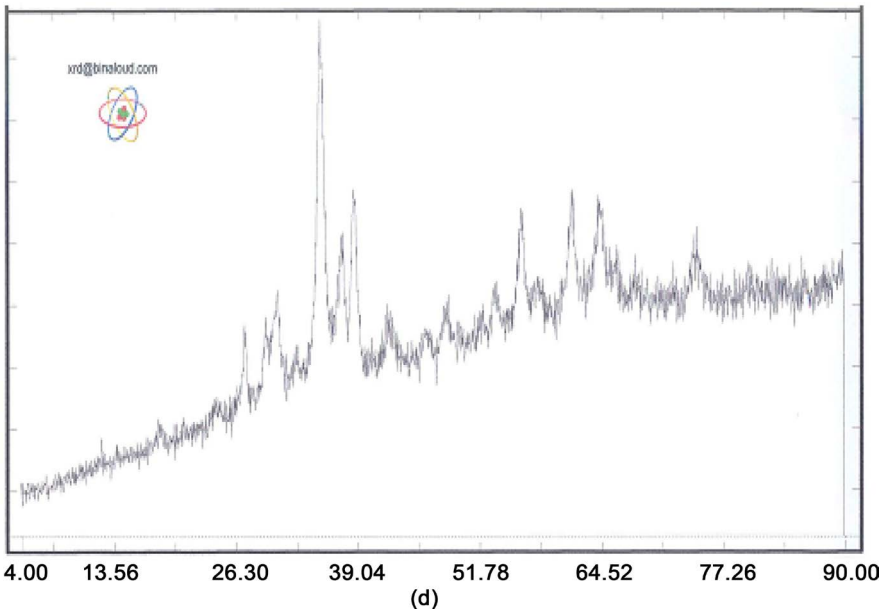


Figure 7. XRD results. (a) Cu phase synthesis in acidity of 3.32; (b) CuO phase synthesis in acidity of 5; (c) $CuCr_2O_4$ phase in acidity of 7; (d) $CuO.CuCr_2O_4$ phase in acidity of 9.

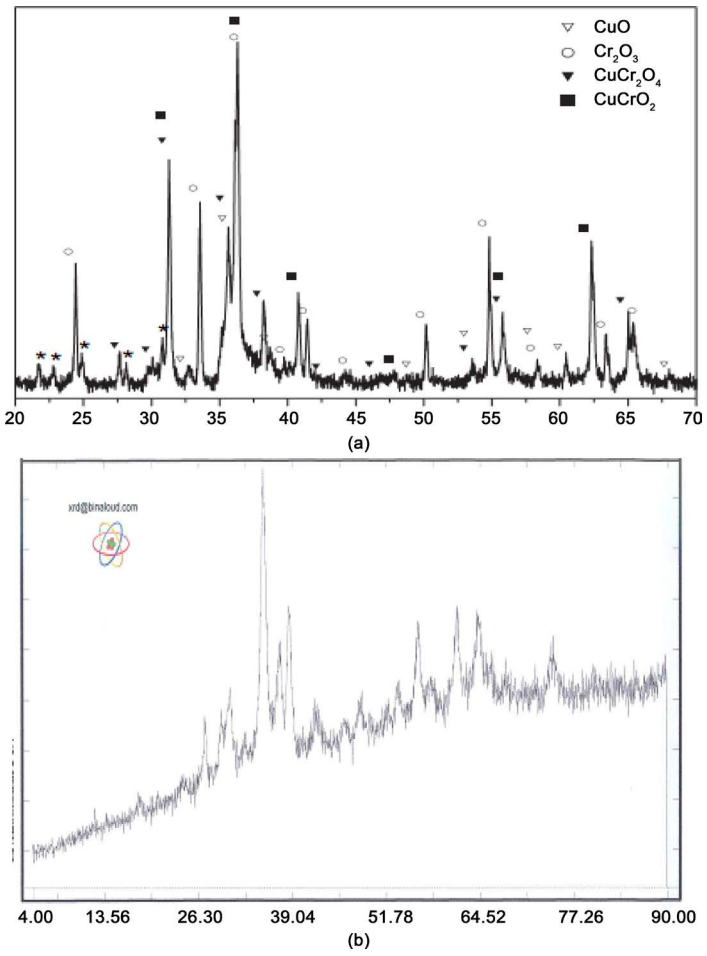


Figure 8. XRD results of last and introduced optimum methods (a) last optimum method; (b) Introduced optimum method in this paper.

phase controlling [8]. We informed in this project that changing PH is effective in type of solid phase. It has done for different calcination temperature and metal ratio, leads to finding the optimum calcination temperature and metal ratio. By this method, the best values for calcination temperature is 700˚C for 3 hrs and Cu to Cr ratio of 0.5. **Figure 8** shows the XRD results analysis of synthesized catalyzer by last optimum method and introduced method of this paper. Also shows that introduced optimum method (calcination temperature of 700˚C for 3 hrs and Cu to Cr ratio of 0.5 in PH of 9) synthesis the single phase catalyzer and there isn't other phases like Cr_2O_3 or $CuCrO_2$.

6. Final Conclusion

Producing Cu-Chromite catalyzer according to applications in solid fuels is important for burning rate catalyzer. Thermal analysis shows that Citrate gel have self-burning behavior and sol-gel method can be used because of low costs, ease of action and uniform particle size for producing nano Cu-Chromite.

References

[1] Liu, T., Wang, L., Yang, P. and Hu B. (2008) Preparation of Nanometer $CuFe_2O_4$ by Auto-Combustion and Its Catalytic Activity on the Thermal Decomposition of Ammonium Perchlorate. *Journal of Materials Science Letters*, **62**, 4056-4058. https://doi.org/10.1016/j.matlet.2008.04.081

[2] Patron, L., Pocol, V. and Carp, O. (2001) New Synthetic Route in Obtaining Copper Chromite(I): Hydrolysis of Some Soluble Salts. *Materials Research Bulletin*, **36**, 1269-1276. https://doi.org/10.1016/S0025-5408(01)00615-8

[3] Patil, P.R., Krishnamurthy, V.N. and Joshi, S.S. (2008) Effect of Nano-Copper Oxide and Copper Chromite on the Thermal Decomposition of Ammonium Perchlorate. *Propellants, Explosives, Pyrotechnics*, **33**, 266-270. https://doi.org/10.1002/prep.200700242

[4] Tagliaferro, F.S., Fernandes, E.A.N., Bacchi, M.A., Campos, E.A., Dutra, R.C.L. and Diniz, M.F. (2006) INAA for Validation of Chromium and Copper Determination in Copper Chromite by Infrared Spectrometry. *Journal of Radioanalytical and Nuclear Chemistry*, **269**, 403-406. https://doi.org/10.1007/s10967-006-0398-9

[5] Sitthisa, S., Sooknoi, T., Ma, Y., Balbuena, P.B. and Resasco, D.E. (2011) Kinetics and Mechanism of Hydrogenation of Furfural on Cu/SiO 2 Catalysts. *Journal of Catalysis*, **277**, 1-13. https://doi.org/10.1016/j.jcat.2010.10.005

[6] Prasad, R. and Pratichi, S. (2011) Applications and Preparation Methods of Copper Chromite Catalysts: A Review. *Bulletin of Chemical Reaction Engineering & Catalysis*, **6**, 63-113. https://doi.org/10.9767/bcrec.6.2.829.63-113

[7] Roy, S. and Ghose, J. (1999) Synthese and Studies on Some Copper Cchromite Spinel Oxide Composites. *Materials Research Bulletin*, **34**, 1179-1186. https://doi.org/10.1016/S0025-5408(99)00109-9

[8] Wei, L. and Hua, C. (2007) Synthesis and Characterization of Cu-Cr-O Nanocomposites. *Journal of Central South University of Technology,* **14**, 291-295. https://doi.org/10.1007/s11771-007-0057-5