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Pouresmaeily Seyed Mohammad
Department of Chemistry & Chemical Engineering, Malek-e-Ashtar University of Technology, Shabanlou, Iran

Shahidzadeh Mansour
Department of Chemistry & Chemical Engineering, Malek-e-Ashtar University of Technology, Shabanlou, Iran

H Shirkavand Behzad
Institute for Color Science & Technology, Shams, Iran

Ebrahimi Sobhan
Department of Material Science and Engineering, Sharif University of Technology, Azadi Ave, Tehran, Iran

Corresponding Author:
Pouresmaeily Seyed Mohammad
Department of Chemistry & Chemical Engineering, Malek-e-Ashtar University of Technology, Shabanlou, Iran

Synthesis of nano metric Cu-Chromite catalyzer by Citrate self-burning sol-gel and PH effects study

Pouresmaeily Seyed Mohammad, H Shirkavand Behzad, Shahidzadeh Mansour and Ebrahimi Sobhan

Abstract
It has been introduced several ways for rising fuel burning rate. Using catalyzers is most 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. This paper explains producing this catalyzer by Citrate sol-gel. Thermal analysis is used for studying process and SEM and XRD images for determination of particle sizes.

Keywords: Nano Cu-Chromite, Citrate sol-gel, catalyzer

Introduction
Accessing high burning rate fuels is one of today needs for military and aero-space industrial purposes. It has been introduced several ways to rising burning rate fuels. Using catalyzer in fuel compound, is one of most common ways. Generally, an intermediate metal especially iron, used for central core of compound such as oxides, chelates and etc. For producing composed solid fuels usually use high oxidant polymer binders with high values of oxidant causes physical and chemical changes of fuel and then reducing lifetime. According to studies, Intermediate metals intensify the oxidation and oxidational degeneration of polymers reactions considerable [1, 2]. Cu-Chromite catalyzer has useful applications in military industries. This substance added to solid fuel containing Ammonium Perchlorate as burning rate catalyzer and cause reducing Ammonium Perchlorate decomposition temperature, consequence rising burning rate. This catalyzer is produced by several methods such as: ceramic, sol-gel, coprecipitating and vacuum precipitating. Ceramic and coprecipitating are most common methods among the others and now macro- producing of this catalyzer done by these methods.

Ceramic method
By this method Cu and Cr oxides mixed together then calcinate for 6hrs[6] in 900 ˚C in acetone (as solvent) [3].

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

Co-precipitation method
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 [4]

$$2CuSO_4(aq) + K_2Cr_2O_7(aq) + 4NH_3 + 3H_2O \rightarrow 2Cu(OH)NH_4CrO_4(s) + K_2SO_4(aq) + (NH_4)_2SO_4(aq)$$

$$2Cu(OH)NH_4CrO_4(s) \xrightarrow{110\text{-}500\ ^\circ C} CuO_{(}s) + CuCr_2O_4(s) + 5H_2O$$

Vacuum precipitating is a laboratory method, that isn't economical because of problems of performing such as: low temperature, high vacuum for producing catalyzer [5].

By studying different factors: ease of perform, low costs, uniform particle size, Citrate sol-gel was choice for producing catalyzer [6].

Empirical section

Thermal decomposition process acts with thermal analysis of DTA/TG [7] model SAT1649 device with heating rate 10 °C /min in air. Solid phases detects with XRD [8] device, model Xpert-Philips with CuKα radiations. Outcome Chromite nano particles calcinated sizes measures with SEM [9] images of Philips-Xl30 model device.

Catalyzer fabrication

First add 0.01mole of Cu-nitrate and 0.01 mole Cr-nitrate into deionized water, produces metal Nitrate. Then add 100 ml Citric acid 2 molar in to metal Nitrate slowly and carefully that it takes 30 mins [10] in 50 ˚C. After that heat the reaction container to 95 ˚C till water vaporize slowly and viscous gel make. Then heat the gel to 160 ˚C in 2 hrs till a black powder appears, finally by calcination of the black powder in 600 ˚C and 2 hrs till nano Cu-Chromite catalyzer produces.

Results and Discussion

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.Figure1 shows that in DTA diagram, exothermic reaction acts in 237 ˚C. This reaction is because of reduction-oxidation reactions between Citrate system and Nitrate. 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.

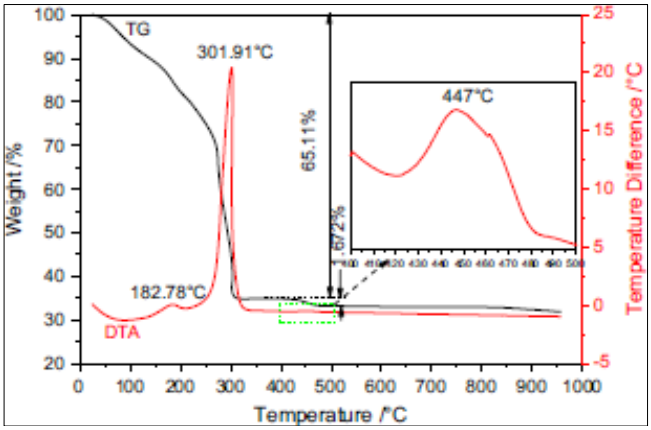

Fig 1: Thermal analysis diagram

Phase analysis and particle size determination

Figure 2 shows that ash produces as result of drying in 160 ˚C then calcination in 600 ˚C, includes different oxides of Cu and Cr compounds. In figure 2, also figure 3 shows nano particle sizes which measured with SEM.

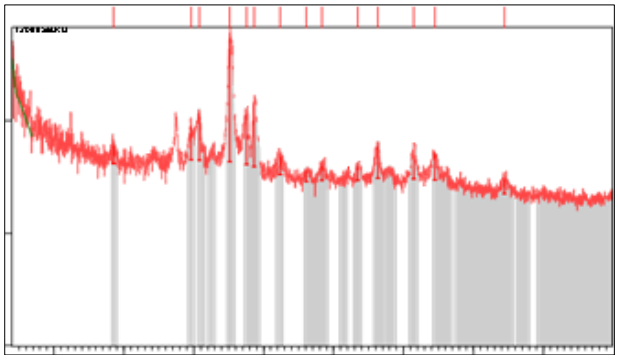

Fig 2: XRD results

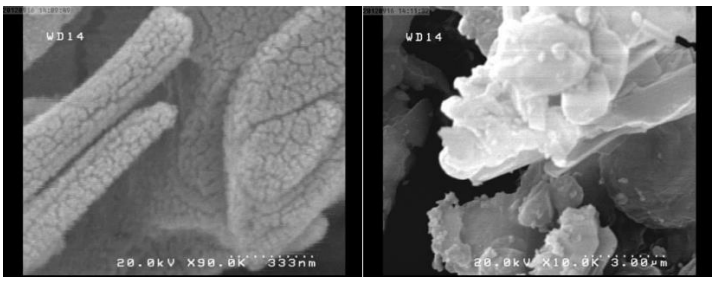

Fig 3: SEM images

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 ($CuO.CuCr_2O_4$) (Figure 4). The peak of 1637cm^{-1} is for CuO vibrations. Existing solid phase ($CuO.CuCr_2O_4$) can proved by spectrum data. Reported studies compatibility the empirical data with FT-IR spectrums by Miller and Willkins for mineral onions [7].

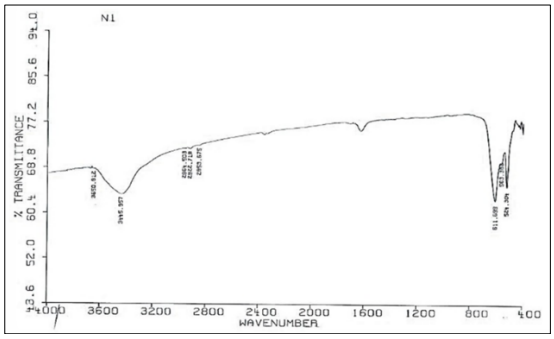

Fig 4: Ft-Ir test results for produced particles

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 [11] 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.

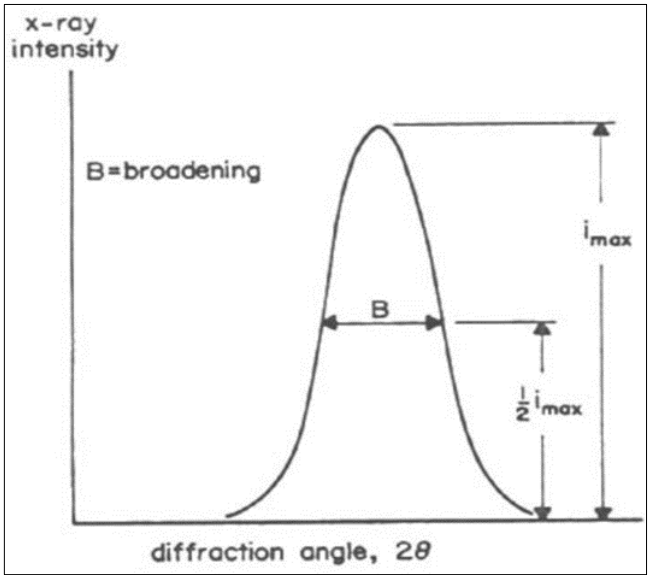

Fig 5: FWHM method

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

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing	Rel. Int. [%]	Tip width [°2Th.]	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

Measuring and determining synthesized productions crystalline type by TEM images

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

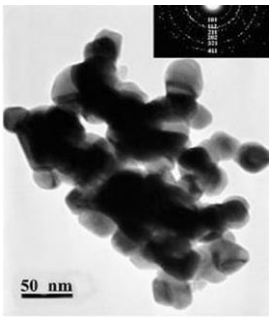

Fig 6: TEM images of synthesized nano catalyzer sample

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.

Table 2: Cu-Chromite synthesized samples in different PHs

Sample No.	Cu-Cr ratio	Citric acid to total metals molar ratio	Drying	Calcintating	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

Effect of PH is because of formation of complex of metals and Citrateion. 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. Type of synthesized complex, stable ability amount and thermal decomposition method are effective in phase of solid produced. In different PHs, synthesis different metal complexes 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 85nm.Results shows that by determining a specific PH could specify the desired type of solid-phase catalysts (Figure 7)

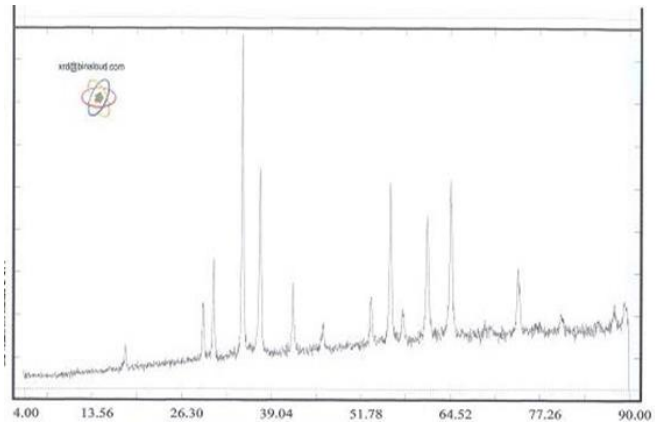

Fig 7a: Cu phase synthesis in acidity of 3.32

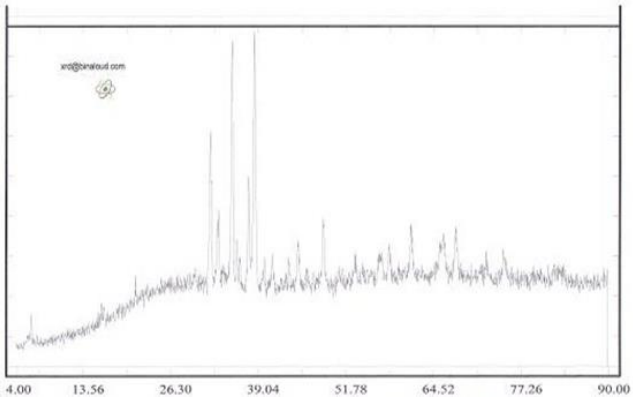

Fig 7b: CuO phase synthesis in acidity of 5

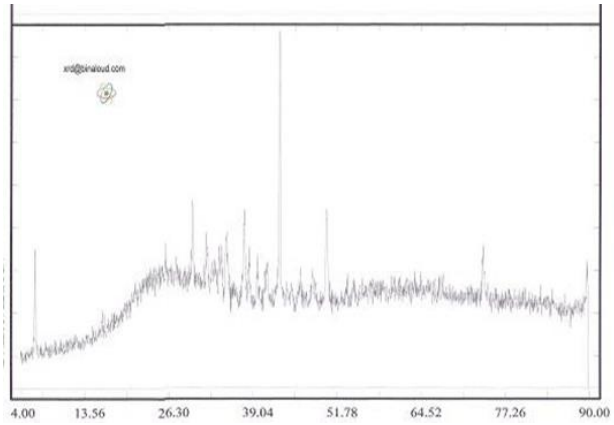

Fig 7c: CuCr2O4 phase in acidity of 7

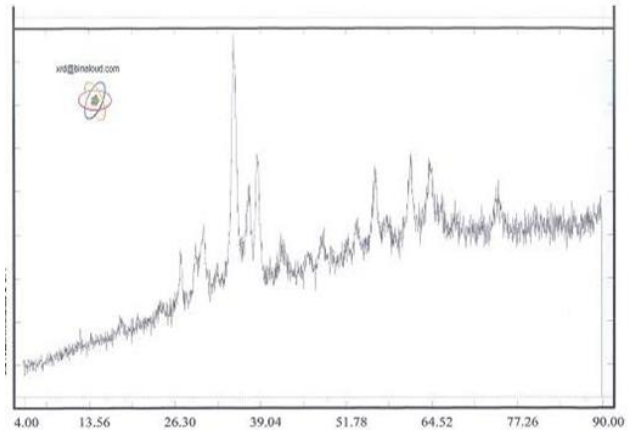

Fig 7d: CuO.CuCr2O4 phase in acidity of 9

Fig 7: XRD results

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.

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 represents the main consisting phase of particles. Last researches in sol-gel Citrate were based on studying calcination temperature and metals ratio for phase controlling. 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 [8]. 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 $CuCrO_2$.

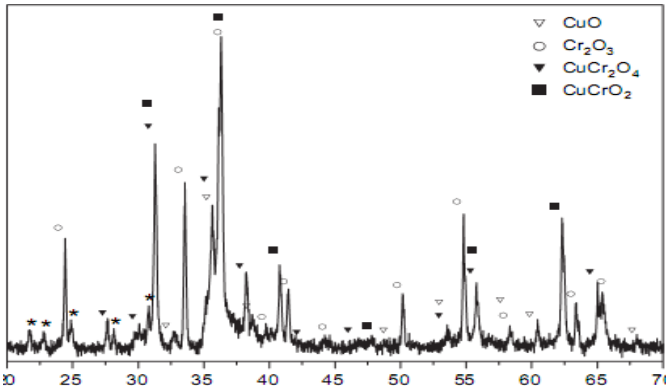

Fig 8a: last optimum method

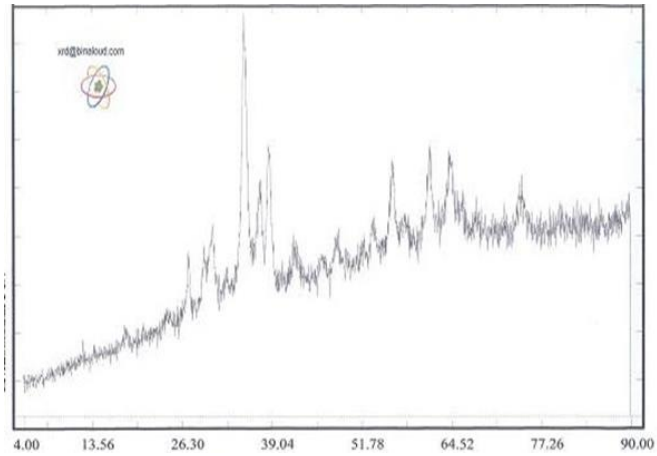

Fig 8b: Introduced optimum method in this paper

Fig 8: XRD results of last and introduced optimum methods

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 used because of low costs, ease of action and uniform particle size for producing nano Cu-Chromite.

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