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Cu-Chromite burning rate catalyst synthesis study

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Abstract
Cu-Chromite catalyst used in military industries has very benefits. This article contains a solid fuel burning rate of Ammonium Perchlorate as a catalyst and decompose Ammonium Perchlorate by decreasing temperature and increasing the burning rate. According to importance and usage benefits, the catalysts with different methods is made of Cu-Chromite catalyst introduced in this paper.

Keywords: Cu-Chromite, Co-precipitation method, Ceramic method, Sol-gel, micro emulsion

Introduction

Accessing high burning rate fuels is one of today's needs for strategic military purposes and aerospace industries. Introduced several ways to increase the burning of fuels. The most common one used in the composition of the fuel burning rate catalysts. The burning rate usually is an intermediate metal catalyst, especially as the central core of iron oxide compounds including, chelates, etc. It used usually high oxidant polymeric compound as binder. Using high values of oxidant in long times causes physical and chemical changes and reducing lifetime. According to researches, transition metals intensify oxidation and polymers degeneration significantly. Cu-Chromite catalyzer is an important catalyzer in chemical reactions and uses in different reactions such as: hydrogenation, dehydrogenation, hydrogenolysis, oxidation, alkylation, and cycloadding, also as catalyzer for removing extra organic compounds from water, volatile organic compounds, burning rate catalyzer for composite fuels. Also uses in reforming processes for producing hydrogen. Cu-Chromite also uses in alcohols converting by removing sulfur in water thermochemical cycle, producing hydrogen from methanol, alcohol synthesis by CO to CO_2 converting in thermal decomposition of biomasses, pharmaceutical productions, synthesis of a variety of fragrances and aromatic chemicals industry, sulfur treatment, the production of electrodes, sensors and semiconductor manufacturing heat- resistant pigments. It has done too much researches and projects in producing and application of this catalyzer, also there are too much handbooks and inventions about this subject. So there are several studies on innovation preparing methods and exploitation usage on Cu-Chromite catalyzer. Nonetheless, it’s continue different and alternative studies on new methods of producing and presenting now. Table 1 shows the general properties of Cu-Chromite [1].

Table 1: General properties of Cu-Chromite

Chemical formula	Cu2Cr2O4
Scientific number	01101-01-9
Molecular weight	163.54
Boiling temperature	Unknown
Smelting temperature	Unknown
Solution in water	Low
Physical state	Solid
Ignition point temperature	Unknown
Appearance form	Black powder
Density	$1.38 gr.cm^{-3}$

1-Cu-Chromite catalyzer synthesis methods

Catalyzer shows several properties when using different synthesis methods even use one primary materials. Crystalize amount, surface properties and special surface amount of crystal are factors that determines the catalyzer activity and they are related to synthesis methods. There are several methods for Cu-Chromite synthesis:

1) Ceramic method
2) Co-precipitation method
3) Ammoniac Cu Oxalate Chromate thermal decomposition method
4) Hydrothermal method
5) Nano-metric distribution method
6) Micro emulsion method
7) Sonochemical method
8) Chemical reduction method
9) Sol-gel method

1-1-Ceramic method

By this method Cr and Cu Oxides react together in Acetone then calcinate in 900 ˚C for 6 hrs[6], finally Cu-Chromite produces. Kawamoto and his colleagues synthesized Cu-Chromite by mixing Cu(II) and Cr(III) with three different Cu to Cr ratios of: 0.61,1 and 1.5 [2]. Oxide mixture homogenize By Acetone and calcinates in 900 ˚C for 6hrs.

$$CuO(s) + Cr_2O_3 \xrightarrow{\text{6 hrs, 900 ˚C}} CuCr_2O_4$$

1-2-Co-precipitation method

By this method, add Ammonium Hydroxide (NH_4OH) to 0.5mole of Ammonium Dichromate ($(NH_4)2Cr_2O_7$) in 500 ml of water for changing the yellow color of solution to orange. Permitted to solution to isotherm with room temperature then add 1mole of Cu-Nitrate 3water crystalized ($Cu\ (NO_3)_2.3H_2O$) and 30 ml of water, then solution mixed. Produced red-brown precipitate, is Basic Copper Ammonium Chromate ($Cu\ (OH)\ NH_4CrO_4$) that filtered and dried for 12 hrs in 100-110 ˚C. This material changes into powder and then transferred to crucible and decomposed by Bunsen burner. After starting the thermal decomposition, Chromate decomposition begins because of adequate reaction temperature. Crucible then heated in free flame till smoking and its contents took black and fully powder in this step, it should carefully mix the contents continuously for preventing of thermal concentration in a point. Then cool the products to room temperature and suspension in 200 ml of Acetic-Acid of 10% purity. This suspension filtered and washed by water several times and dried for 12 hrs in 100-110 ˚C for taking powder. Kawamoto and his colleagues synthesized the catalyzer by co-precipitation of water solution of ($CuSO_4.5H_2O$ and $K_2Cr_2O_7$) in presence of Ammoniac when mole ratio of Cu to Cr is 0.3 to 0.5 [3]. Related reactions is below:

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

110−500 ˚C

$$2Cu(OH)NH_4CrO_4(s) \rightarrow CuO(s) + CuCr_2O_4(s) + 5H_2O$$

1-3-Ammoniac Copper Oxalate Chromate (ACOC) thermal decomposition

ACOC ($CuNH_3C_2O_4NH_4CrO_4$) uses for synthesis of Cu-Chromite. This intermediate composition produced by mixing of Cu-Oxalate Ammoniac solution (CuC_2O_4) and Ammonium-Chromate ($(NH_4)_2CrO_4$) with 1:1 ratio following that solvent vaporizing and drying the product in 105 ˚C. Green dried complex reserves for a time in desiccator in presence of Calcium-Chloride($CaCl_2$). Intermediate products are solvable in aqueous solution of Ammoniac. Catalyzer created by calcination of intermediate compound in air and Argon gas in 350 ˚C [4]. General decomposition is so exothermic:

$$2CuNH_3C_2O_4NH_4CrO_4 + 2O_2 \rightarrow CuO.\ CuCr_2O_4 + 4CO_2 + 2N_2 + 7H_2O$$

Decomposition in Argon is less exothermic:

$$2CuNH_3C_2O_4.\ NH_4CrO_4 \rightarrow Cu.\ CuCr_2O_4 + 2NH_3 + 4CO_2 + N_2 + 4H_2O$$

The environment of calcination of intermediate products is effective on decomposition mechanism, then consequence chemical composition and physical properties of final compound. Extreme exothermic of decomposition in air ($CuOCr_2O_4$) cause reduce the active surface of catalyzer respect to decomposition in Argon ($Cu.CuCr_2O_4$). So decomposition in Argon cause synthesis a new catalyzer that reduce the reaction steps.

1-4-Hydrothermal method

Hydrothermal method being considered for advanced material production processes recently. Because of its advantages for synthesis of nano structure materials for extended usages like: catalyzer, ceramics, biomaterials, nano composites, electronic industries and others. From of advantages of this method can point, high purity and homogeneity, symmetry of crystals, different nano particles size production ability and low environmental harms respect to other processes. George and Sugunan used this method for synthesis of nano Cu-Chromite catalyzer in this way that Provide a mixture of 10% of Cu-Nitrate, Ni-Nitrate and Cr-Nitrate for synthesis of compounds like $Cu1\text{-}XNiXCr_2O_4$ (that X=0.25,0.5,0.75) with suitable mole ratio. Then heat the mixture to 70-80 ˚C and add Ammoniac solution of 15% drop by drop and mixing the mixture homogeneously till acidity fix to 6.5-8. The precipitate hold for 2 hrs in this temperature then filtered and washed with water. Finally dried in 110 ˚C for 24 hrs and calcinated for 8hrs in 650 ˚C. Arboleda and his colleagues synthesized new Cu-Chromite compound with formulation of $(NH_4)1.5Cu_2Cr_2O_8(OH)1.5\text{-}\ H_2O$ by hydrothermal method. This compound decomposed after 600 ˚C calcination to $CuCr_2O_4$ [5].

1-5-Nano casting method

Common methods for synthesis of mixed Oxides, usually produces infinite intermediate compounds that participate directly in calcination steps. This method motivate product in high temperatures that reduces (chemical) the active surface of products. By using this method synthesis of nano materials occurs in limit environment and a porous mold. Attractivity of this method is that limits the calcination methods and lets particle size controlling with adjusting of synthesis conditions so produces the favorable nano particles. Genrally this method consist of two steps:

1) Nano structure mold providing
2) Filling the pores of mold with intermediate compound, following that crystallizing the voids of mold then removing the mold.

Liang showed that Carbon molds are able to synthesis of Cu-Chromite catalyzer with high surface area that has high activity and selectivity [6]. The synthesis of catalyzer method in following: About 3 gr of Carbon that saturated with 15 ml of aqueous solution of Cr-Nitrate and Cu-Nitrate with mole different ratios in 30 mins[7]. Then filters till its water fully removed from Carbon surface for not producing large Oxide particle. After drying in air and 70 ˚C for a night time transform contents in to the tube of Quartz and heat resistance then transfer in to furnace. Temperature of furnace should rise, 1 ˚C per minute till reach the final temperature. The atmosphere is Argon to 300 ˚C and then changes gradually to 20% of O_2 and Argon with speed of 12 ml per minute. In 550 ˚C Carbon mold removes in air for 8 hrs. Conveting from Cu-Nitrate and Cr-Nitrate in to active catalytic Cu-Oxide and Cr-Oxide acts by efficiency of 100% and ratio of Cu to Cr is related to first ratio in solution.

1-6-Micro emulsion method

Cu-chromite nano structure particles produced by Kumar and his colleagues by micro emulsion method in presence of Poly Vinyl Pyrrolidone (PVP) (as supporter polymer) in different sizes [7]. By this method, produces two micro emulsions from $Cu(NO_3)_2$ and $KCr(CN)_6$ by PVP and then mixed together till Cu- Chromite nano structures particles depose, this particles washed by Acetone. The ratio of concentration of PVP to Cu ion for nano particles control is 20 to 200.

1-7-Chemical reduction method

This method is a suitable method for synthesis of amorphous nano structure catalytic materials by simple primary materials. Liaw synthesized Cu-Chromite catalyzer by chemical reduction of 0.1molar of Cu- Nitrate in 1 molar of Sodium-Boron Hydride aqueous solution [8]. Sodium-Boron Hydride aqueous solution added to Cu-Nitrate aqueous solution by micro pump in Hydrogen gas atmosphere. Cr reduces by coprecipitating process and Sodium-Boron Hydride and add adequate Cr-Nitrate salt to that in presence of Cu-Nitrate aqueous solution. Produced black precipitates dried and calcinated. They used catalytic properties of catalyzer for hydrogenation of Olefins, Carbonyls and twofold link systems, also they compared them with commercial Cu-Chromite catalyzers. Results showed that fine Cr-CuB catalyzers that contain less than 5% mole of Cr are more active than commercial samples that contains more than 50% mole of Cr. Suggested that this catalyzers, are suitable catalyzers for substituting of Cu-Chromite for liquid phase hydrogenation.

1-8- Sonochemical method

By this method, Cu-Acetate and K-Chromate saluted in Ammoniac solution and heated in 65 ˚C simultaneous with magnetic heater mixing. By destroying Ammoniac, wash materials with Acetone in two steps and finally putting them into ultrasonic device to producing catalyzer [9-10].

1-9-Sol-gel method

The purpose of sol-gel method at low temperature chemical processes to produce objects, films, fibers, particles or composites of form and appropriate level that can be used commercially after the completion of a stage. Traditional processes leads to produce materials which have micro structures about 1-100 µm. By sol-gel can produce the micro structure of materials in 1-100nm.Sol-gel process performs in three ways:

1) Citrate sol-gel
2) Alkoxide sol-gel
3) No Alkoxide sol-gel

1-10-Citrate sol-gel

First, by mixing 0.01 mole of Cu-Nitrate with 0.03 mole of Cr-Nitrate then shake them after 30 mins and add Citric Acid while the mole ratio of Acid to total metal is 2:1 then heat in 85 ˚C in different times till black gel produces. Then put the gel into dish for 3 hrs and then calcinate that in 600 ˚C till catalyzer produces [11].

1-11-Alkoxide sol-gel method

This method is based on polymeric intermediates for producing Spinels and provides stoichiometric controls for several producing of materials. Metallic Nitrate solutions mixed to Citric Acid with specific stoichiometric ratios. The solution mixed for 1 hrs on a hot surface and temperature is 70 ˚C, then heated up to 900 ˚C and in this temperature, Ethylene Glycol added with weight ratio of 40:60 to Citric Acid. Temperature fixed till resin produce that in 300 ˚C takes polymer. The intermediate powder calcinates in different temperatures of 400-900 ˚C for 4 hrs or in 900 ˚C for 8 hrs. Spinel structure crystalize begins with calcination in 700 ˚C. $CuCr_2O_4$ is the only present phase in calcination in 900 ˚C. The recently process is similar to last method, just metallic Nitrate salute in Alcohol instead of water. The main weakness point of this method is sensibility in humidity and disability of using commercial intermediates for metallic Oxides [12].

1-12- No Alkoxide sol-gel method

This method contains hydrolysis and metallic salts densifications, by avoiding weakness point of last method (high sensibility of humidity) although the deference weakness point of hydrolysis is different parts of material. The strength of this method is that important reductions that relate to calcination temperatures, prevents of agglomeration of nano metric particle [13]. The way of synthesis of Cu-Chromite catalyzer by this method is: Salute 3.2 gr of Cr $(NO_3)_3.9H_2O$ and 1gr of Cu $(NO_3)_2.3H_2O$ in 16ml of Ethanol in 60 ˚C till a black-blue transparent solution produce. After adding 5ml of Propylene Oxide, by rotating the solution, a black-green transparent solution produces. After drying for a night in 70 ˚C, transfer the solution to a heat resistance Quartz dish and then to furnace. The furnace temperature should rise 1 ˚C per minute then fix in 120 ˚C and 20% of O_2 in Argon and 120 ml per minute flow. The efficiency of Cr and Cu Oxides in catalyzer is about 100% and the final ratio of Cu to Cr depends on primary materials mole fraction. Results shows that area surface of catalyzer sets by Cu to Cr ratio and temperature conditions.

2-Feasibility study of selecting method for producing Cu-Chromite catalyzer as burning rate catalyzer

There are different parameters for comparing methods including: type of catalyzer (the catalyzer uses in military industries is of CuO, $CuCr_2O_4$), industrial scale feasibility, ease of perform, uniform particles distribution and economic efficiency that shown in table 2.

Table 2: Comparing methods of producing of Cu-Chromite catalyzer

Produce method	Industrial feasibility	Ease of perform	Catalyzer type	Uniform particles distribution	Produce cost
Ceramic	Ok	Easy	Cu Cr_2O_4	High	Cheap
Co-precipitation	Ok	Hard	CuO, Cu Cr_2O_4	High	Partly expensive
ACOC Thermal decomposition	Ok	Hard	Cu Cr_2O_4	Low	Cheap
Hydrothermal	Fail	Easy	Cu $Cr2O_4$,Cr_2O_7	High	Cheap
Nanocasting	Fail	Hard	Cu Cr_2O_4	Good	Expensive
Micro emulsion	Ok	Hard	Cu Cr_2O_4	High	Expensive
Sonochemical	Fail	Hard	CuO, Cu Cr_2O_4	Good	Expensive
Chemical reduction	Ok	hard	Cu Cr_2O_4، Cr	Low	Expensive
Sol-gel	Ok	Easy	CuO, Cu Cr_2O_4	Good	Cheap

As observes in table 2, co-precipitation, sonochemical and sol-gel produce CuO, Cu Cr_2O_4 type of catalyzer. Because of several reactions and lack of precision control, Co-precipitation method is a lack of ease method. Also Sonochemical method is able to produce favorable catalyzer, but it isn't a feasible industrial method. According to remarks, sol-gel is a suitable method. This method have several advantages including: ease of perform, uniform particles distribution, low costs and most importance, type of catalyzer (CuO, Cu Cr_2O_4).

3-Conclusion

Cu-Chromite is an important catalyzer in chemical reactions and uses in different reactions like: hydrogenation, dehydrogenation, hydrogenolysis, oxidation, alkylation, cycloaddition, also as catalyzer for reduce the extra organic compounds from water, producing volatile organic compounds, and burn rate catalyzer in fuels and results were satisfying. There are different ways to producing this catalyzer, the most important ways are ceramic, co-precipitation, Ammoniac Cu-Chromite Oxalate compounds thermal decomposition, hydrothermal, nanocasting, micro emulsion, sonochemical, chemical reduction and sol-gel. For comparing the producing methods, studying parameters such as: catalyzer type, industrial feasibility, ease of perform, uniform particles distribution and economical efficiency of producing costs. By studying the mentioned articles among the ways of producing this catalyzer, sols-gel is a suitable method for synthesis of catalyzer as fuels burn rate catalyzer.

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