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Process intensification of copper chromite ($CuCr_2O_4$) nanoparticle production using continuous flow microreactor

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ABSTRACT

The present study deals with the production of monodispersed copper chromite nanoparticles in a continuous flow micro channel reactor. The precursors used were aqueous solutions of copper nitrate and chromium nitrate. A mixture of the precursor at a fixed copper to chromium metal ion ratio and citric acid were infused in a continuous flow microreactor maintained at a constant temperature of 80 °C and followed by calcinations at 200 °C for a fixed duration of 2 h to yield the nano powder. The effect of different Cu/Cr metal ion ratios on the particle size was studied. The optimum value of flow rate and Cu/Cr ratio was found to be 75 and 0.5 mL/h, respectively. The particle size of obtained copper chromite nanoparticles was measured to be in the range 192–300 nm, relatively smaller compared to that obtained in a batch reactor. The effect of different types of surfactants on the particle size was also studied and it was observed that the surfactants played an important role in controlling nucleation during particle formation and subsequent growth of the particles.

1. Introduction

Microfluidic devices are process intensifying devices, which offer several advantages over batch processes for the production of nanoparticles. The large surface area to volume ratio of microreactors offers enhanced heat and mass transfers in comparison with conventional batch reactors. This intensification occurs in microfluidic devices mainly because of control over heat transfer and effective mixing due to the reduced characteristic time of the transport processes. Moreover, efficient mixing is a key advantage in preparing narrow size distribution of nanoparticles in microreactors. In all, microreactors offer many opportunities for exploring and developing novel nanoparticle synthesis routes. Therefore, nanoparticles with a certain particle size, uniform size distribution, and desired structure can be generated through efficiently controlled reactions in microreactors [1–4].

Copper chromite ($CuCr_2O_4$) has a wide range of commercial applications such as, catalysts in hydrogenation, dehydrogenation, hydrogenolysis, oxidation, alkylation etc. [5–12]. In addition, it has been used in various composite solid propellants as an efficient combustion supporting catalyst in the domain of space vehicles and weapon industries. The size and shape of copper chromite particles affect the catalytic activity as observed in the case of burning rate of propellant and effect of propellant concentration (burning rates of hydroxyl terminated polybutadiene (HTPB)/diethylhexyl adipate (DOA) and the effect of Al particle concentration, size and shape) [7]. Sathishkumar et al. [7] attempted the synthesis of nano sized copper chromite by a solution combustion process using citric acid and glycine as fuel. Pure spinel phase copper chromite ($CuCr_2O_4$) was synthesized. The reaction time for the synthesis with glycine was lower compared to that with citric acid. Ceramic and co-precipitation methods are widely used for the production of copper chromite. In both the methods, the presence of impurities, which mainly comprise of mixed oxides, and side reaction are important issues. Copper chromite for its use as a catalyst should be in its purest form along with high specific area and narrow distribution of particle size. Li and Cheng [5] suggested that Cu–Cr–O nanocomposites can be prepared via a citric acid (CA) complexation approach. The results showed that well-crystallized Cu–Cr–O nanocomposites could be produced after the calcination of CA–Cu–Cr precursors at 500 °C for 3 h. The authors also suggested that the phase composition of Cu–Cr–O nanocomposites

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depends on the molar ratio of Cu to Cr in the starting reactants. Mohan et al. [12] have used a new route, which bypasses precipitation as well reduction steps of traditional copper chromite catalysts preparation. The duration for catalyst preparation was considerably reduced.

Further, several researchers have used the microreactor system for the preparation of different products. Torigoe et al. [13] studied the effect of hydrodynamic parameters (capillary diameter, linear flow rate, volume flow rate, and reaction temperature) and concentrations (precursor and stabilizer) on the average particle size. It can be inferred that the particle size can be controlled by varying linear flow rate and temperature as well as precursor concentration ratio. Jeevaratinam et al. [14] have studied the effect of gas and liquid flow rates on the size distribution of barium sulphate nanoparticles precipitated in a two phase flow capillary microreactor. It has been reported that with an increase in the flow rate of any of two streams, the mean particle size of barium sulphate product gets decreased. Increased mixing and higher Ba^{2+} ion concentrations in the small microreactor shift rates in favor of nucleation as compared to agglomeration, yielding smaller particles in the product. Zhao et al. [15] have studied different categories of nanoparticles manufactured in microreactors to highlight the wide application of microfluidic systems in the development of novel nanomaterials. Continuous flow microreactors also exhibit a number of advantages, such as simple operation, high throughput, easy control, and high temperature adaptability. However, some inherent disadvantages, including broad size distribution due to poor mixing and clogging or cross-contamination due to the direct contact with channel walls limit their application. Köhler et al. [16] studied the formation of colloidal solutions containing metal nanoparticles at different ratios of silver and gold in microreactors in order to investigate the possibility of preparing such nanoparticles under micro-flow-through conditions. The catalytic activity of the obtained nanoparticles and nanostructured precipitates was evaluated by bleaching of organic dyes with potassium peroxodisulphate. A significant enhancement of bleaching rate was reported in the case of silver, palladium and iron-containing catalyst nanoparticles. It is widely concluded that microfluidic methods offer a possibility to control the mean particle size and distributions with varying operational parameters such as flow rate, tube diameter and residence time [17]. Patron et al. [18] studied the possibility of obtaining copper chromite through thermal decomposition of polynuclear coordination compounds $[Cr_2Cu(NH_3)_2(OH)_6](NO_3)_2$ and $[Cr_2Cu(OH)_8]\cdot 4H_2O$ which were obtained through hydrolytic decomposition of chromium and copper soluble salts. The decomposition of the coordinate compounds yielded a pure tetragonal Cr_2CuO_4 with mean crystallite sizes varying in the range 133–210 Å in the temperature limits 823–1073 K.

In this study, efforts were made for the first time to prepare copper chromite nanoparticles in a continuous microreactor system along with surfactants. The effect of ratios of Cu/Cr with citric acid on the particle size was studied. The reaction was carried out in a small capillary reactor having an inner diameter of 0.8 mm. Furthermore, the effect of reactor parameter such as residence time on average particle size was also studied.

2. Experimental

2.1. Materials

AR grade copper nitrate hexahydrate ($Cu(NO_3)_2\cdot 6H_2O$) with 98% purity and chromium nitrate nonahydrate ($Cr(NO_3)_3\cdot 9H_2O$) and citric acid were purchased from SD Fine Chemicals, Mumbai, India. AR grade polyvinylpyrrolidone K30 ($M_W = 40{,}000$), polyethylene glycol ($M_W = 570–630$) and cetyl trimethyl ammonium bromide (CTAB) were procured from Merck Specialties Pvt., Ltd., Mumbai, India. All the chemicals were used as received.

2.2. Experimental setup and procedure

Infuser pumps (Universal Medical Instruments, Indore, MP) and syringes (Dispovan make, volume = 50 mL) were used for experiments. Tube made of linear low density polyethylene tube (LLDPE) with an internal diameter of 0.8 mm and a length of 200 cm was used as microreactor. Deionized water (conductivity less than 1 μS) was used for the preparation of aqueous solutions of precursors. Different molar solutions of copper nitrate and chromium nitrate were prepared with various molar ratios of copper to chromium as shown in Table 1A. A dilute solution of surfactant was used for the preparation of the copper and chromium nitrate. A set of different surfactants was chosen to study their effect on the particle size of the nanoparticles and to identify the best surfactant (Table 1B).

As shown in Fig. 1, a syringe was filled with the mixture of copper and chromium nitrate solutions in the ratio as reported in Table 1A, while an aqueous solution of citric acid in a molar ratio of 2:1 with respect to the total metal ion concentration was taken in another syringe. The microreactor was kept in a water bath at a temperature of 80 °C as shown in Fig. 1. The flow rate ranged from 25 to 150 mL/h. The solution obtained at the end of reaction was a complex of Cu–Cr–CA and was greenish in color. Calcination of obtained greenish material was carried out at a temperature of 200 °C for 2 h during which the greenish aqueous solution gradually became viscous and released a reddish brown gas. Further, the slurry formed a porous mass of green color which burned with small intensity red sparks at the bottom of the vessel to form the crispy flakes of ash burnt copper chromite.

Table 1A
Cu/Cr ratio and surfactant concentrations used in different experiments.

Sample identification	Cu/Cr ratio	Surfactant added (mg/100 mL of solution)	Flow rate	Number of experiments conducted
1	0.1	0	50	10
2	0.3	0	50	8
3	0.5	0	50	8
4	0.7	0	50	8
5	0.9	0	50	10
6	0.9	PVP 2 mg	50	8
7	0.9	PVP 2 mg	25	8
8	0.9	CTAB 2 mg	50	8
9	0.9	CTAB 2 mg	25	8
10	0.1	0	75	10
11	0.1	0	100	8
12	0.1	0	150	8
13	0.9	0	25	8
14	0.9	0	75	8

Table 1B
Details of the repeated experiments and the particle size obtained in the respective experiments.

Sr. No.	Flow rate (mL/h)	Cu/Cr ratio	Particle size ror repeated experiments (nm)						Average particle size (nm)
			1	2	3	4	5	6	
1	50	0.1	222.5	240	226	227.6	230.8	–	229.4
2	75	0.1	250.2	251.5	245.2	247.2	251.2	253.5	249.8
3	100	0.1	273.8	278.9	270.6	273.2	–	–	274.1
4	150	0.1	294.6	292.8	291.2	300.2	–	–	294.7
5	25	0.9	297.8	292.5	294.8	–	–	–	295.0
6	50	0.9	248.8	250.2	248.3	257.6	243.6	–	249.7
7	75	0.9	209.3	209.9	211	–	–	–	210.1

Sr. No.	Flow rate (mL/h)	Cu/Cr ratio	Type of surfactant	Particle size for repeated experiments (nm)					Average particle size (nm)
				1	2	3	4	5	
1	25	0.9	PVP	291.4	289.2	293	–	–	291.2
2	50	0.9	PVP	232.8	238.7	232.5	237.9	–	235.5
3	25	0.9	CTAB	249.4	249.6	249.9	248.7	–	249.4
4	50	0.9	CTAB	192	192.3	191.8	195.1	–	192.8

2.3. Characterization of Cu–Cr–nanocomposites

The synthesized copper chromite samples were characterized by FTIR, X-ray diffraction, field emission scanning electron microscopic (FESEM), and particle size analyzer. Wide angle X-ray diffraction analysis of the composites was performed on analytical powder diffractometer (X'Pert PRO) using CuKα radiation ($\lambda = 1.5406$ Å) in reflection mode. Particle size of copper chromite particles were analyzed by Zeta Potential Analyzer (Malvern Zetasizer nano ZS 90). The morphology of copper chromite particles was studied using FESEM (JEOL 7600F) analysis. FTIR analysis of samples was carried out (SHIMADZU 8400S) in the range of 4000–500 cm^{-1}.

3. Results and discussion

3.1. Reaction mechanism of formation of copper chromite in a microreactor

Both metal nitrate precursors undergo hydrolysis and polycondensation reactions (Reactions (1)–(4)) to form a colloidal suspension. The hydrolysis of precursor molecules and the condensation between the resulting reactive species are the essential reactions involved during synthesis of copper chromite. Hydrolyses (1) and (2) are followed by condensations (3) and (4) to form —M—O—M— bonds via dehydration [10]. The dehydration process was performed by calcinations at a temperature of about 200 °C. The solution slowly became viscous over a period of time and color changed gradually from the green to brown where it finally reached an ash burnt state to form the black spindle of copper chromite. Due to the continuous production of the precursors and their coexistence with the other components, these might agglomerate, which was prevented by the addition of surfactant. This facilitated the formation smaller particle sizes as the growth and agglomeration stages were hindered.

The hydrolysis and condensation reaction mechanism is given as follows:

Hydrolysis reaction

$$\text{Cu(NO}_3)_2 \rightarrow \text{Cu}^{2+} + 2\text{NO}_3{}^{-}$$

$$\text{Cr(NO}_3)_2 \rightarrow \text{Cr}^{3+} + 3\text{NO}_3{}^{-}$$

Citric acid = CA

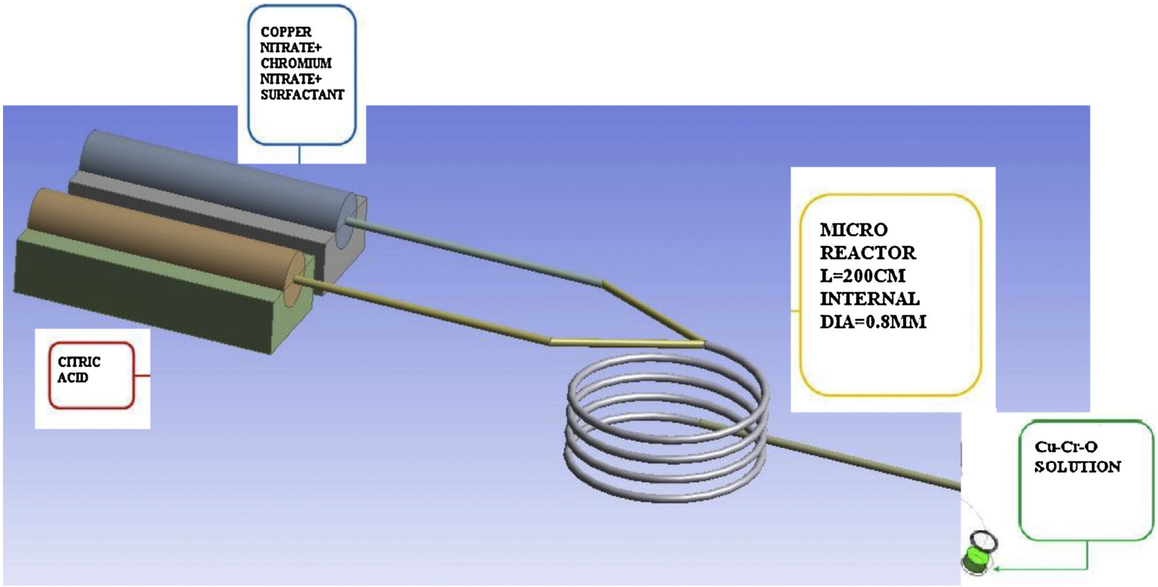

Fig. 1. Experimental setup of microreactor for preparation of copper chromite nanoparticles.

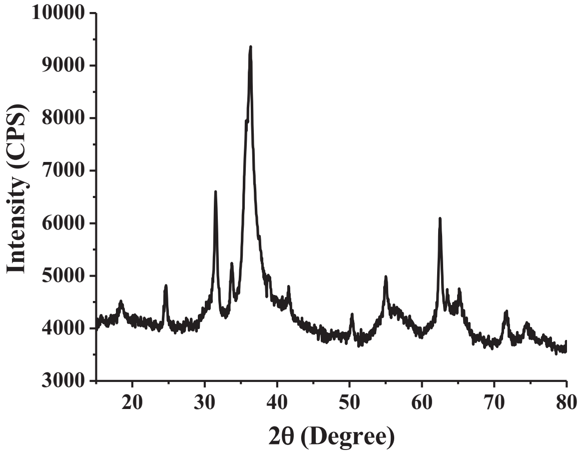

Fig. 2. XRD pattern of copper chromite sample (Cu/Cr ratio = 0.7) prepared in the absence of a surfactant.

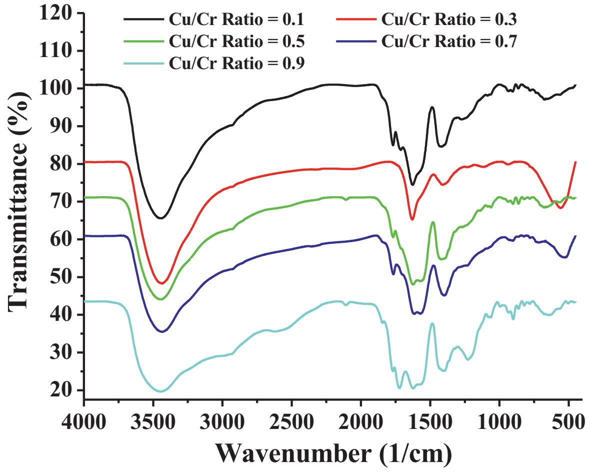

Fig. 3. FTIR spectrum of prepared copper chromite samples at different ratio of Cu/Cr.

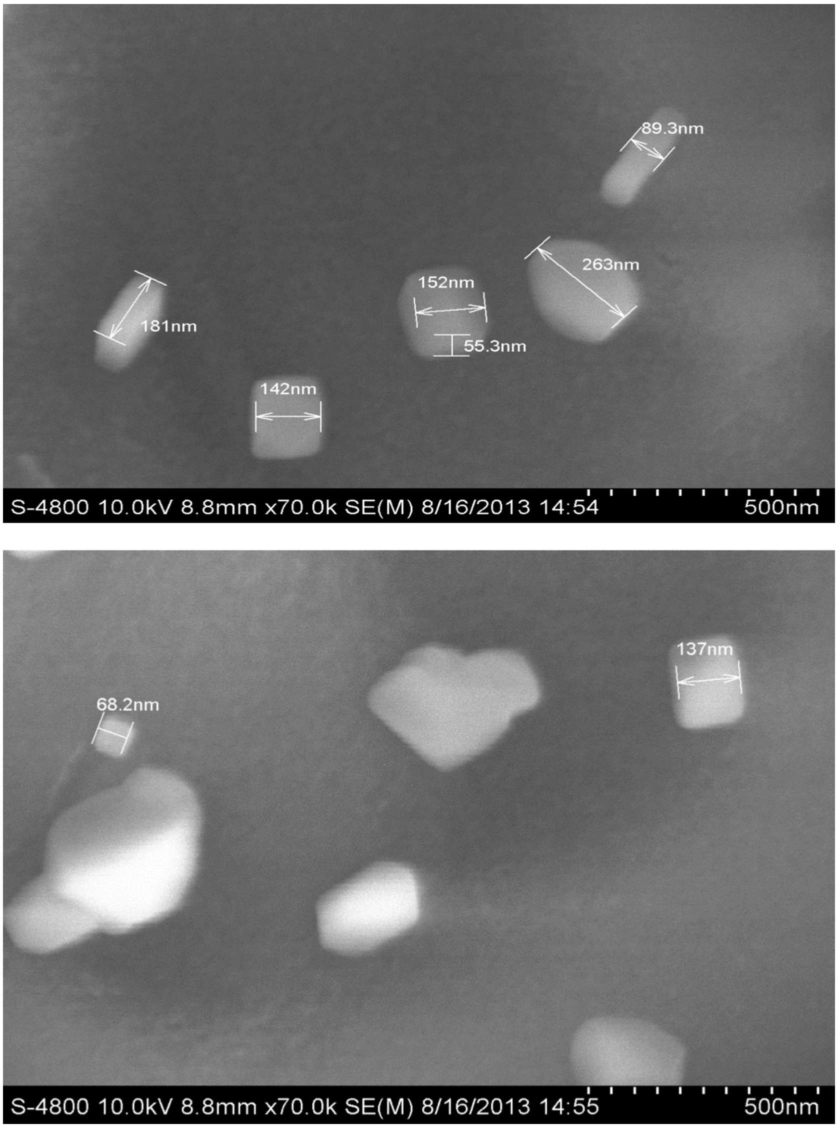

Fig. 4. FESEM images of copper chromite sample at Cu/Cr ratio = 0.3 and 50 mL/h flow rate.

$Cu^{2+} + CA \rightarrow [Cu(CA)]^{2+}$

$H_2O \rightarrow H^+ + OH^-$

$2Cr^{3+} + [Cu(CA)]^{2+} + 6OH^- + 2NO_3^- \rightarrow [Cr_2Cu(CA)(OH)_6](NO_3)_2]$
(Precursor A) (1)

$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3$

$Cr^{3+} + Cr(OH)_3 + Cu^{2+} + 5OH^- + 4H_2O \rightarrow [Cr_2Cu(OH)_8]\cdot 4H_2O$
(Precursor B) (2)

$14H^+ + 14NO_3^- \rightarrow 14HNO_3$

Polycondensation by dehydration
Precursor A

$[Cr_2Cu(CA)(OH)_6](NO_3)_2 \rightarrow [Cr_2Cu(OH)_6](NO_3)_2 + CA$

$[Cr_2Cu(OH)_6](NO_3)_2 \rightarrow Cr_2CuO(OH)_6 \rightarrow Cr_2O_2(OH)_2\cdot CuO + 2H_2O$

$Cr_2O_2(OH)_2\cdot CuO \rightarrow Cr_2O_3\cdot CuO + H_2O$

$Cr_2O_3\cdot CuO \rightarrow CuCr_2O_4$ (black spinel) (3)

Precursor B

$[Cr_2Cu(OH)_8]\cdot 4H_2O \rightarrow Cr_2Cu(OH)_8 + 4H_2O$

$Cr_2Cu(OH)_8 \rightarrow Cr_2O_2(OH)_2CuO + 3H_2O$

$Cr_2O_2(OH)_2CuO \rightarrow Cr_2O_3\cdot CuO + H_2O$

$Cr_2O_3\cdot CuO \rightarrow CuCr_2O_4$ (black spinel) (4)

Cu–Cr–O nanocomposites were synthesized by varying the Cu to Cr ratio with citric acid as the fuel and with the addition of different surfactants such as PVP and CTAB. The X-ray diffraction pattern of Cu/Cr ratio 0.7 sample 4 (Table 1A) without the addition of surfactant is depicted in Fig. 2. The higher peak at 36.39° depicted the presence of $CuCrO_2$ (JCPDF: 01-074-0983) and the sharp diffraction peak indicated the crystalline structure of $CuCrO_2$. The peak at 2θ value of 33.83° indicated the presence of small amounts of Cr_2O_3 (JCPDF: 00-006-0504). The formation of $CuCrO_2$ was attributed to calcination temperature, which had an effect on the structure and composition of $CuCrO_2$. The higher temperature causes the delafossite phase compound of $CuCrO_2$ [9].

Fig. 3 shows FTIR spectrum of prepared copper chromite nanoparticles. Copper chromite is expected to exhibit the characteristic bands in the region around 690–650 cm^{-1}, 580–540 cm^{-1}, and 530–485 cm^{-1} due to Cu—O and Cr—O stretching frequencies, respectively. The IR band in the range 600–540 cm^{-1} observed for all chromite samples could be attributed to stretching vibration of Cr—O bands of chromium of chromium atoms in the tetragonal environment of the O atom [19]. As depicted in Fig. 3, the characteristic peaks of the $CuCr_2O_4$ sample at 691 and 515 cm^{-1} could be attributed to the presence of $Cr_2O_4^{-2}$ group and characteristic peak at 884 cm^{-1} referred to Cr—O chromate group. The bands between 1200–1500 cm^{-1} (Cr_2O_3) and 3300–3500 cm^{-1} (water) were attributed to the residual precursor materials in the final product obtained. In this case, for $CuCr_2O_4$, the vibration frequency at 691 cm^{-1} is a characteristic of Cu—O stretching nodes of the octahedral sites [19]. Further synthesis of $CuCr_2O_4$ particles was carried out at different ratio of Cu/Cr and its spectrums are reported in Fig. 3. Besides the characteristic peaks of $CuCr_2O_4$, additional peaks can be attributed to the reagents used in the synthesis of $CuCr_2O_4$ particles.

The morphological study of copper chromite nanoparticles prepared in the microreactor with Cu/Cr ratio = 0.3 for flow rate 50 mL/h is depicted in Fig. 4. The distinct cubical morphology of copper chromite nanoparticles of particle size in the range of 69–263 nm is observed. The obtained size of copper chromite nanoparticles is attributed to the use of the microreactor system in which the residence time of the reaction mixture is considerably decreased in comparison to a batch process, hence appreciable crystal growth of copper chromite nanoparticles is restricted. It is also attributed to the reduced growth time which leads to formation of smaller sized copper chromite nanoparticles [20].

3.2. Effect of flow rate on the size of precursor onto copper chromite

The reaction was carried out using four different flow rates (50, 75, 100 and 150 mL/h) and the temperature of the precursors was kept constant at 80 °C. For the metal ion ratio (Cu/Cr) equal to 0.1, it is observed from Fig. 5(A) that the particle size of the copper chromite nanoparticle increases in size with an increase in the flow rate (Table 1B). This increase in the size may be attributed to the

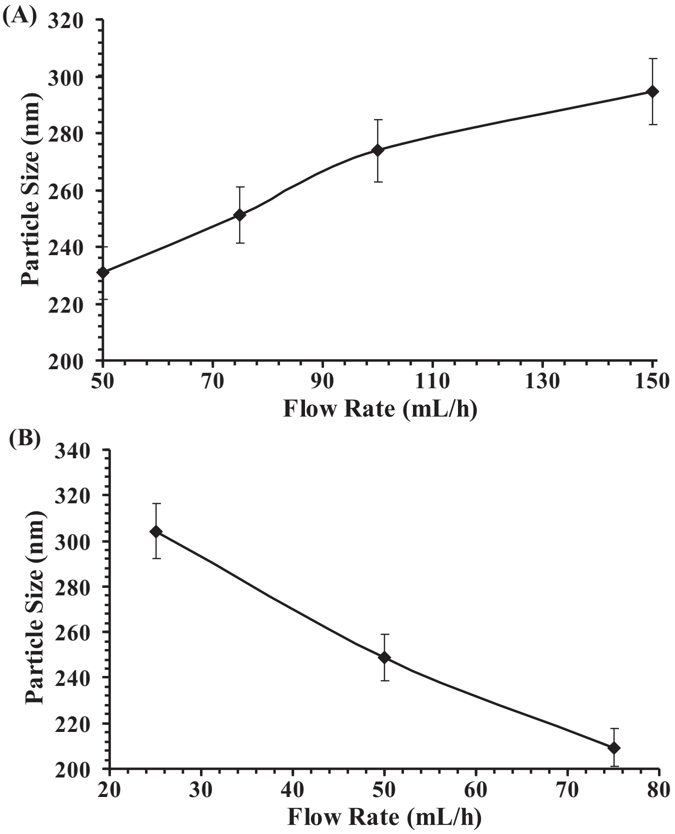

Fig. 5. Effect of flow rate on copper chromite particle size at (A) Cu/Cr ratio = 0.1 and (B) Cu/Cr ratio = 0.9.

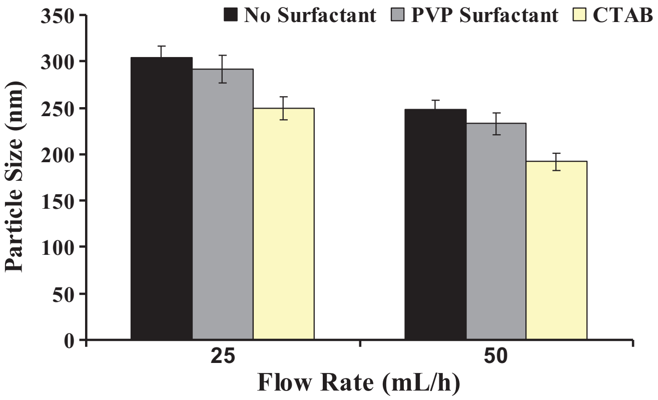

Fig. 6. Size of copper chromite particle at different flow rates for without surfactant, CTAB and PVP at Cu/Cr ratio = 0.9.

low concentrations of one of the reactants resulting in a lower nucleation rate and a higher growth rate. At low reactant concentrations, an increase in the flow rate would increase the interactions between the particles which cause agglomeration leading to an increase in the particle size. The effect of flow rate on the average particle size of copper chromite was also studied at higher a concentration, i.e., Cu/Cr ratio = 0.9. It was observed from Fig. 5(B) that the copper chromite particle size decreases with an increase in the flow rate (Table 1B). The reason for this behavior is the shorter residence time during which the rate of nucleation is higher and the growth rate is slower.

3.3. Effect of the surfactant on the size of the nanoparticles

The experiments were conducted at a Cu/Cr ratio = 0.9, using different flow rates of the precursors along with surfactant type in order to study the effect on the particle size of copper chromite nanoparticles. The concentration of the surfactant used was about 2 mg/100 mL copper and chromium nitrate solution. The flow rate of the each of the precursor was maintained at 25 mL/h and 50 mL/h in two different experiments. Further, the surfactant concentration was maintained at 2 mg/100 mL in copper and chromium nitrate solutions. Considerable effect on the particle size of copper chromite nanoparticles could be expected with an increase in the flow rate of the copper and chromium nitrate solutions in the presence of the surfactant. The trend observed for the effect of PVP and CTAB on the particle size is depicted in Fig. 6 and Table 1B. It is clear that the surfactants inhibit the growth and agglomeration of the particles, therefore, reduction in the size of copper chromite nanoparticles is observed. The particle size of the copper chromite nanoparticles without the addition of surfactant at 25 mL/h flow rate is 304.3 nm. It is reduced to 291.4 nm with the addition of PVP and to 249.9 nm when CTAB is used. At 50 mL/h flow rate, the particle size of copper chromite nanoparticles reduces from 248.8 to 232.8 nm with the addition of PVP and to a value of 192 nm with the use of CTAB. The experimental error observed in these experiments is less than 5%. In the present study, the effect of the flow rate on the particle size is found to be significant. It is attributed to the shorter residence time with an increase in the precursor flow rate which results in the formation of smaller size particles with reduced agglomeration [21]. Further, as PVP is non-ionic surfactant, therefore, the size of the copper chromite nanoparticles size is observed to be larger as compared to CTAB. In the case of CTAB, the copper chromite nanoparticles are expected to be covered on surface by positively charged CTA head groups leading to electrostatic repulsion between the formed particles thus avoiding the cluster formation.

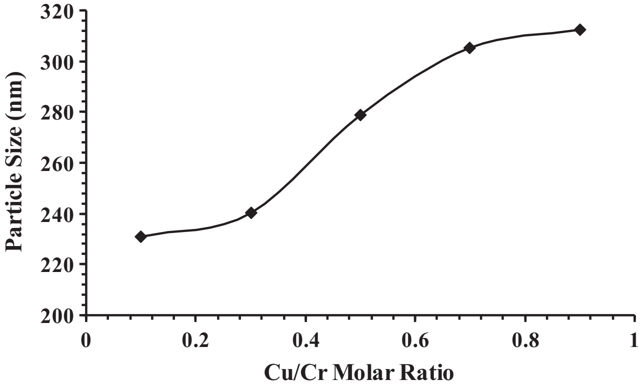

Fig. 7. Effect of Cu/Cr ratio on average size of copper chromite particles.

3.4. Effect of Cu/Cr ratio on particle size

The reaction was carried out at five different precursor ratios (Cu/Cr ratio of 0.1, 0.3, 0.5, 0.7 and 0.9) keeping the citric acid to metal ion ratio constant. The reaction temperature was kept constant at 80 °C for all the metal ion ratios and the flow rate was kept constant at 50 mL/h. It is observed from Fig. 7 that the particle size of copper chromite nanoparticles increases with an increase in the Cu/Cr ratio. At higher Cu/Cr ratio, the formation of larger copper chromite nanoparticles takes place. In the first stage, nucleation rate increases with an increase in the concentration. In the second stage, the growth of these particles takes place by agglomeration.

Table 2 demonstrates the differences in the duration of the procedure and the operating conditions of various processes reported for the production of copper chromite. In regular co-precipitation methods the reaction is operated at about 300 °C and calcination is carried out in the temperature range between 600 and 900 °C. In comparison, the duration of calcinations, as reported in Table 2, is reduced remarkably when microreactor based synthesis process is used. Regular co-precipitation methods operate for duration of about 6 h to form the ash burnt particle followed by another hour for hot drying to produce copper chromite whereas the microreactor synthesis requires 1 h of heating at 80 °C followed by calcination duration of about 2 h at 200 °C. It can thus be concluded that the continuous process not only needs reduced calcination duration, but also the temperature required for the calcination is greatly reduced. The benefit of the continuous process is also evident from production of smaller sized copper chromite nanoparticles as compared to the other processes.

Table 2
Comparisons of different batch processes with the current continuous microreaction based process.

Sr. No	Name of the process (reference)	Reaction duration and temperature	Calcination duration and temperature
1	Co-precipitation method [7]	2 h, 160–180 °C	700 °C for 3 h
2	Citric acid(CA) complexing method [5]	95 °C for several hours + 160 °C for 2 h	600 °C for 3 h
3	Microreactor process	1–2 h at 80 °C	200 °C for 2 h

4. Conclusions

The production of copper chromite particles has been carried out successfully using the microreactor based process. It can be concluded that the processes occurring in microreactor resulted in smaller particle size as compared to the other co-precipitation methods. The significant reduction in the reaction temperature indicates a higher heat transfer coefficient of the microreactor. Also, it was observed that the duration of calcinations process reduced remarkably in the microreactor based synthesis process. The particle size increases with an increase in the flow rate at low concentrations, whereas the particle size decreases with an increase in the flow rate at higher Cu/Cr ratio which is a normal behavior because of a decrease in the residence time. The surfactant considerably reduced the growth rate of particles which resulted in a decrease in particle size even with the increase in flow rates. The optimum range of Cu/Cr ratio is between 0.3 and 0.5. A higher ratio of Cu/Cr increases the particle size of copper chromite nanoparticles. In this study, effects of the fuel, variation in the Cu/Cr ratio, the calcination process and its temperature conditions during preparation process and its influence on the properties such as phase purity and size/shape of copper chromite nanoparticles have been explored. Further, during scaling up of the microreactor system, one can use multiple reactors for industrial large scale production. However clogging of micro-channels is a major issue in microreactor system, which needs further optimization.

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