CSM
Chemistry of Solid Materials
Vol. 1 No. 1 2013

# A comparative study on the dispersion of CuO-ZnO-$Al_2O_3$ nanoparticles over HZSM-5 via batch co-precipitation, semibatch co-precipitation and combined co-precipitation-ultrasound methods

**R. Khoshbin, M. Haghighi**[*]
*Ph.D Student and Associate Professor, Chemical Engineering Faculty, Reactor and Catalysis Research Center (RCRC), Sahand University of Technology, Sahand New Town, Tabriz, Iran.*
** Corresponding author's E-mail: haghighi@sut.ac.ir*

(Received: June 2013, Accepted: July 2013)

## ABSTRACT

A series of CuO-ZnO-$Al_2O_3$ nanoparticles over HZSM-5 were successfully prepared using different methods of batch co-precipitation, semibatch co-precipitation and combined co-precipitation-ultrasound. Nitrates of copper, zinc and aluminum were used as precursors, while Na-ZSM-5 was employed as composite support and sodium carbonate was used as precipitant agent. The effects of preparation methods on physicochemical properties of synthesized nanoparticles were studied using XRD, BET, FESEM, FTIR and TGA-DTG techniques. Furthermore, the formation mechanism of nanosized CuO-ZnO-$Al_2O_3$ over HZSM-5 was proposed. The formation of nanosized CuO-ZnO-$Al_2O_3$ over HZSM-5 with homogeneous grain size was addressed after calcination at 350°C for 5 hr. The results indicated that the crystalline structure, thermal gravimetric behavior and surface morphology of the nanocomposite were strongly dependent on preparation methods. The combined co-precipitation-ultrasound method had superior control in crystallite size and CuO-ZnO-$Al_2O_3$ dispersion. This method resulted in many small grains with almost spherical shapes and narrow particle size distribution.

**Keywords**: ZnO-CuO-$Al_2O_3$, HZSM-5, Nanoparticle, Co-precipitation, Ultrasound.

## 1. INTRODUCTION

An increasingly growing interest in nanostructured inorganic materials has been reported because of their distinct properties from bulk materials. The nanocomposite material can prove optical, electronic and chemical properties in various applications [1-4]. The nanotechnology influenced many chemical engineering fields such as catalysis, separations, drug delivery systems and integration of miniaturized systems such as microreactors [5], fuel cells [6], batteries and sensors [3, 7-9].

Among nanoparticle materials, CuO-ZnO-$Al_2O_3$/HZSM-5 has a great atention because of its wide applications in chemical engineering industries especially in catalytic direct conversion of syngas to dimethyl ether [10-15]. Reported literature reveals that in the most cases this nanoparticle can be prepared via physically mixing of CuO-ZnO-$Al_2O_3$ nanoparticle with HZSM-5 zeolite, co-precipitation and impregnation methods [16-20].

Many applications require nanoparticles with a very exact nano and narrow size distribution. Therefore, development of innovative synthesis methods to control size, morphology and assembly of desired nanostructured material becomes a challenge in this field. Thus, a great number of efforts have been reported to accurate controlling of nanoparticles size with a narrow size distribution. There are many methods of deposition of nano-sized materials over a support such as precipitation [21-24], nitrate combustion [25, 26], sol-gel [27] and sonochemical techniques [28]. Among these methods, the sonochemical technique is considered as an efficient method, since it can produce homogeneous and dispersed nanoparticles without need for expensive instruments and extreme conditions [29-31].

The effect of ultrasound waves can be attributed to the generation, growth and collapse of micro bubbles in the solution [32, 33]. If the cavitations takes place close to the surface of the particles, a jet of liquid penetrate inside the bubble perpendicular to the particles surface leading to formation of high velocity microjet of liquid toward the surface [34, 35].

The aim of this work is a systematic and comparative synthesis of CuO-ZnO$Al_2O_3$/HZSM-5 nanoparticles using three different methods of batch co-precipitation, semibatch co-precipitation and combined co-precipitation-ultrasound methods. The effect of precipitation method and ultrasound on structural properties of nanoparticle was addressed using XRD, BET, FESEM, FTIR and TGA-DTG techniques.

## 2. EXPERIMENTAL

### *2.1 Materials*

Analytical grade chemicals of copper, zinc, aluminum nitrates, as well as sodium carbonate, ammonium nitrate were supplied by Merck and used without further treatment. Na-ZSM-5 with Si/Al = 21 and 300 $m^2/g$ surface area was obtained from SPAG and used after ion exchanged with $NH_4NO_3$.

### *2.2 Nanoparticle Preparation and Procedures*

As shown in Figs. 1-3, preparation of nanoparticle in all methods can be divided into 3 steps. In all methods a HZSM-5 sample was prepared from an original NaZSM-5 powder by repeated ion exchange with $NH_4NO_3$ solutions followed by drying overnight and calcination under air flow at 550ºC for 5 hr (step b in all methods in Figs. 1-3).

### *2.2.1 Batch Co-precipitation*

As illustrated in Fig. 1a, a slurry of HZSM-5 powder (obtained from section b) and metal nitrates ($[Cu^{2+}] + [Zn^{2+}] + [Al^{3+}]=1.0$ M) with molar ratio of Cu:Zn:Al=6:3:1 was prepared. It should be noted that the weight ratio of CuO-ZnO-$Al_2O_3$ to HZSM-5 was kept at 2:1. Then in stage c, batch co-precipitation of metal oxides over HZSM-5 was carried out using drop-wise addition of 1.0 M aqueous solution of sodium carbonate into the metal precursors/support slurry under continuous stirring at 70ºC, until pH of solution reached 7. After aging the mixture for 1 hr under stirring at the same temperature, the resulting precipitates were filtered out and washed three times. The obtained solid was dried at 110ºC overnight and then calcined at 350ºC under air flow for 5 hr.

### *2.2.2 Semibatch Co-precipitation*

The major difference between batch and semibatch methods is in mixing procedures. As shown in Fig. 2 at first stage (a), an aqueous solution containing metal nitrates ($[Cu^{2+}] + [Zn^{2+}] + [Al^{3+}]=1.0$ M) with molar ratio of Cu:Zn:Al=6:3:1 was prepared. Then in stage c, this solution and a 1.0 M aqueous solution of sodium carbonate were drop-wise added simultaneously into the slurry of HZSM-5 powder at constant pH =7.0±0.2 and temperature of 70ºC while continuously stirring. Again the weight ratio of CuO-ZnO-$Al_2O_3$ to HZSM-5 was kept at 2:1. The mixture had been aged for 1 hr under stirring at the same temperature. The drying and calcinations steps were performed as mentioned before.

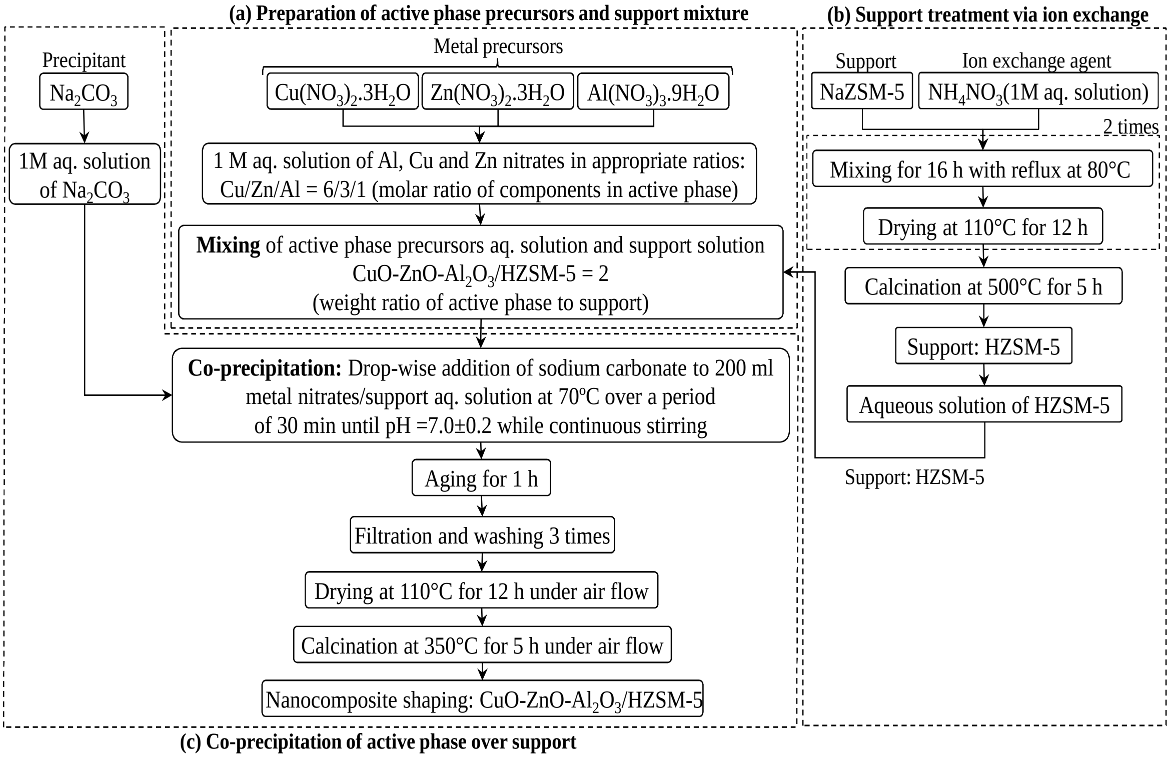

**Fig. 1.** Schematic flow chart for the preparation steps of $CuO-ZnO-Al_2O_3/HZSM-5$ nanoparticle via batch co-precipitation method.

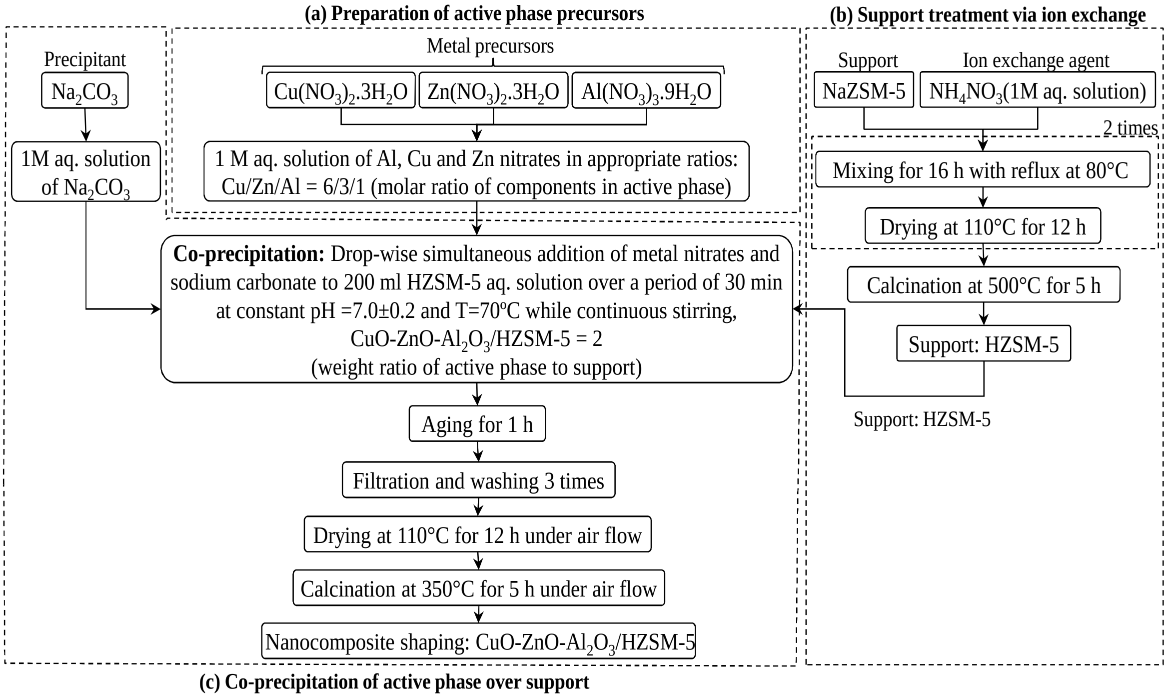

**Fig. 2.** Schematic flow chart for the preparation steps of $CuO-ZnO-Al_2O_3/HZSM-5$ nanoparticle via semibatch co-precipitation method.

### *2.2.3 Combined Co-precipitation-Ultrasound*

In this method co-precipitation process was combined with ultrasound method to enhance metal oxide dispersion over the support. As can be seen in Fig. 3, in first stage (a) the metal oxide solid mixture was prepared using semibatch co-precipitation method. At this stage, a 1.0 M aqueous solution of metal nitrates ($[Cu^{2+}] + [Zn^{2+}] + [Al^{3+}] = 1.0$ M) with molar ratio of Cu:Zn:Al=6:3:1 and 1.0 M aqueous solution of sodium carbonate solution were drop-wise added simultaneously into deionized water at constant pH=7.0 ± 0.2 and temperature of 70ºC while continuously stirring. After the mixture had been aged for 1 hr under stirring at the same temperature, the resulting precipitates were filtered and washed out three times. At final steps of this stage, the solid obtained was dried at 110ºC overnight and then calcined at 350ºC under air flow for 5 hr. At this stage $CuO-ZnO-Al_2O_3$ nanoparticle was prepared. At final stage (c), the synthesized nanoparticle was added to the on HZSM-5 slurry with 2:1 weight ratio and treated by pulsed ultrasound probe (Bandelin). The ultrasound irradiation condition was: 90 W for 45 min in which 600 seconds current pulse time and 30 seconds rest time, in argon atmosphere. The obtained solution was dried at 110ºC overnight and then calcined at 350ºC under air flow for 5 hr**.**

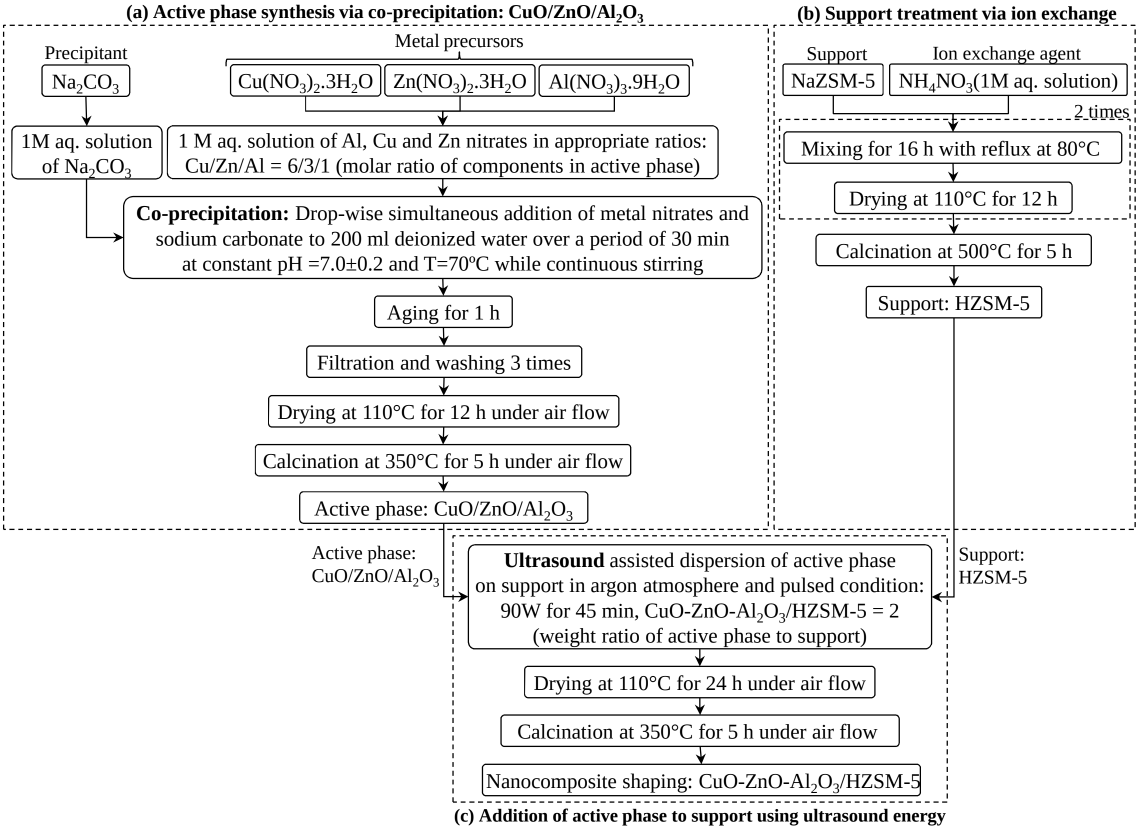

**Fig. 3.** Schematic flow chart for the preparation steps of $CuO-ZnO-Al_2O_3/HZSM-5$ nanoparticle via combined Co-precipitation-ultrasound method.

## *2.3 Nanoparticle Characterizations*

Structural identification and morphological analysis were addressed using powder X-ray diffraction patterns in 2θ range from 5 to 70° using Siemens diffractometer D5000 with monochromatized Cu-Kα radiation at 40 kV and 30 mA. The diffraction pattern was identified using those included in the Joint Committee of Powder Diffraction Standards (JCPDS) data base. The crystal sizes were evaluated from full width at half maximum of the XRD peaks by using Scherrer equation. The microstructure and morphology was studied by field emission scanning electron microscopy (HITACHI S-4160). The surface area of nanoparticles was characterized by nitrogen adsorption and desorption isotherms obtained at -196ºC using a Quantachorom apparatus. Furthermore, the carbonate and nitrate content in each sample was determined gravimetrically by a thermal analysis system (pyris diamond TGA/DTA). The sample temperature was linearly raised from room temperature to 500°C at a rate of 10°C/min under air flow. The carbonate and nitrate content of the testing sample was estimated from the weight loss in the TGA profiles. Finally, FTIR analyses were done by UNI-CAM 4600 Fourier Spectrometer in the range of 400–4000 cm$^{-1}$ using a KBr pellet containing the corresponding sample.

## 3. RESULTS AND DISCUSSION

### *3.1 XRD Analysis*

XRD patterns and average crystallite size of the nanoparticle prepared using different methods are shown in Fig. 4 and Table 1, respectively. Crystallographic analysis showed that intensity of peaks varied in three samples addressing different amount of crystallite phase formed using different methods. Results indicated that the HZSM-5, CuO and ZnO were main components of the nanoparticle, while there were no peaks that can be assigned to $Al_2O_3$. This observation is suggested that $Al_2O_3$ was highly dispersed and/or was amorphous that is in good agreement with previous studies [36].

The HZSM-5 diffraction pattern had peaks at $2\theta$=7.93º and 23.15º indicated that the support had few defects, and a high degree of crystallinity. In the XRD patterns, there were rather strong peaks at $2\theta$=35.6° and 38.9° that can be assigned to CuO and can be indexed to the monoclinic phase of CuO (JCPDS 01-080-1268). The peaks at $2\theta$ =31.96º and 36.25º are ascribed to hexagonal phase of ZnO (JCPDS 01-076-0704). It is observed that the peaks are the most diffused and the peaks of CuO and ZnO had overlap. For example, the peak of ZnO at $2\theta$ of 36.25º is severely covered by the peak of CuO at $2\theta$ of 35.6°.

The width of the diffraction lines of CuO phases in the CuO-ZnO-$Al_2O_3$/-HZSM-5 nanoparticle changed with utilization of different preparation methods. The copper diffraction peaks of the nanoparticles synthesized using combined co-precipitation-ultrasound method became wider and smaller than copper diffraction peak in other preparation methods. This result indicated that the average crystallite size of CuO in this method (7.75 nm) was smaller than those of batch (21.3 nm) and semibatch (14.3 nm) methods. The average crystallite size of ZnO in semibatch co-precipitation and combined co-precipitation-ultrasound methods were very close (~29-32 nm), while using batch co-precipitation method led to increase of average crystallite size (36.1 nm). However, the average crystallite size of ZSM-5 didn't change in all of the methods. In addition, the peak intensity of line in XRD patterns of semibatch co-precipitation and combined co-precipitation-ultrasound methods were less than batch co-precipitation method. These results showed that CuO and ZnO phases in the samples synthesized using semibatch co-precipitation and combined co-precipitation-ultrasound methods were well interacted and dispersed. According to Figueiredo et al. [37], the interaction between CuO and ZnO is an important parameter to determine the catalytic activity of these nanoparticles.

### *3.2 FESEM Analysis*

The morphology of calcined nanoparticles prepared by different methods is shown in Fig. 5. Since morphology of HZSM-5 is cubic, it can be concluded that the CuO-ZnO-$Al_2O_3$ nanoparticle prepared by batch and semibatch co-precipitation methods contains big grains and had lower dispersion in compare of the sample was prepared by combined co-precipitation-ultrasound method. When the ultrasound energy was applied, each particle consists of many small grains whose shapes are almost spherical. The FESEM image of the nanoparticle shows a close contact of CuO-ZnO-$Al_2O_3$ and HZSM-5. This indicates that the ultrasound plays an important role on controlling the morphology of the nanoparticles. Without ultrasonic processing, a mixture of spherical and leaf-like morphology was obtained.

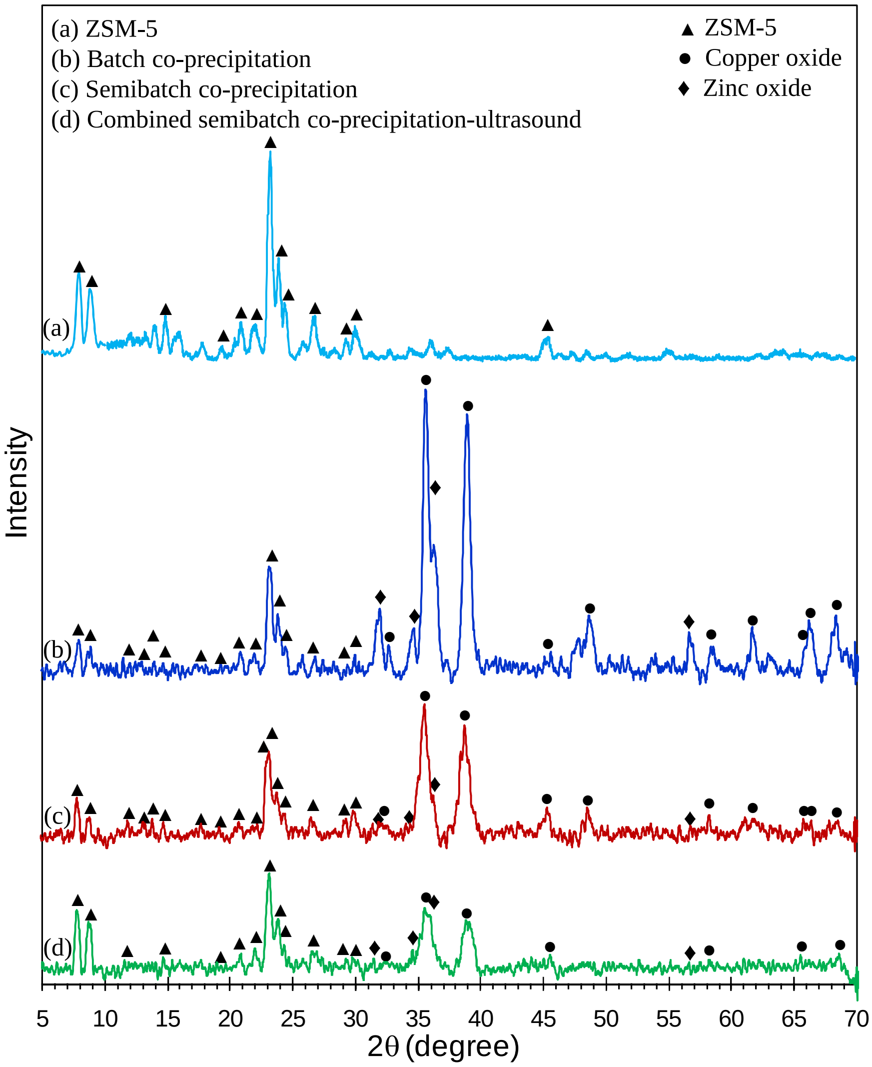

**Fig. 4.** XRD patterns of ZSM-5 (a) and synthesized CuO-ZnO-$Al_2O_3$/HZSM-5 nanoparticles via batch co-precipitation (b), semibatch co-precipitation (c) and combined co-precipitation-ultrasound (d) methods.

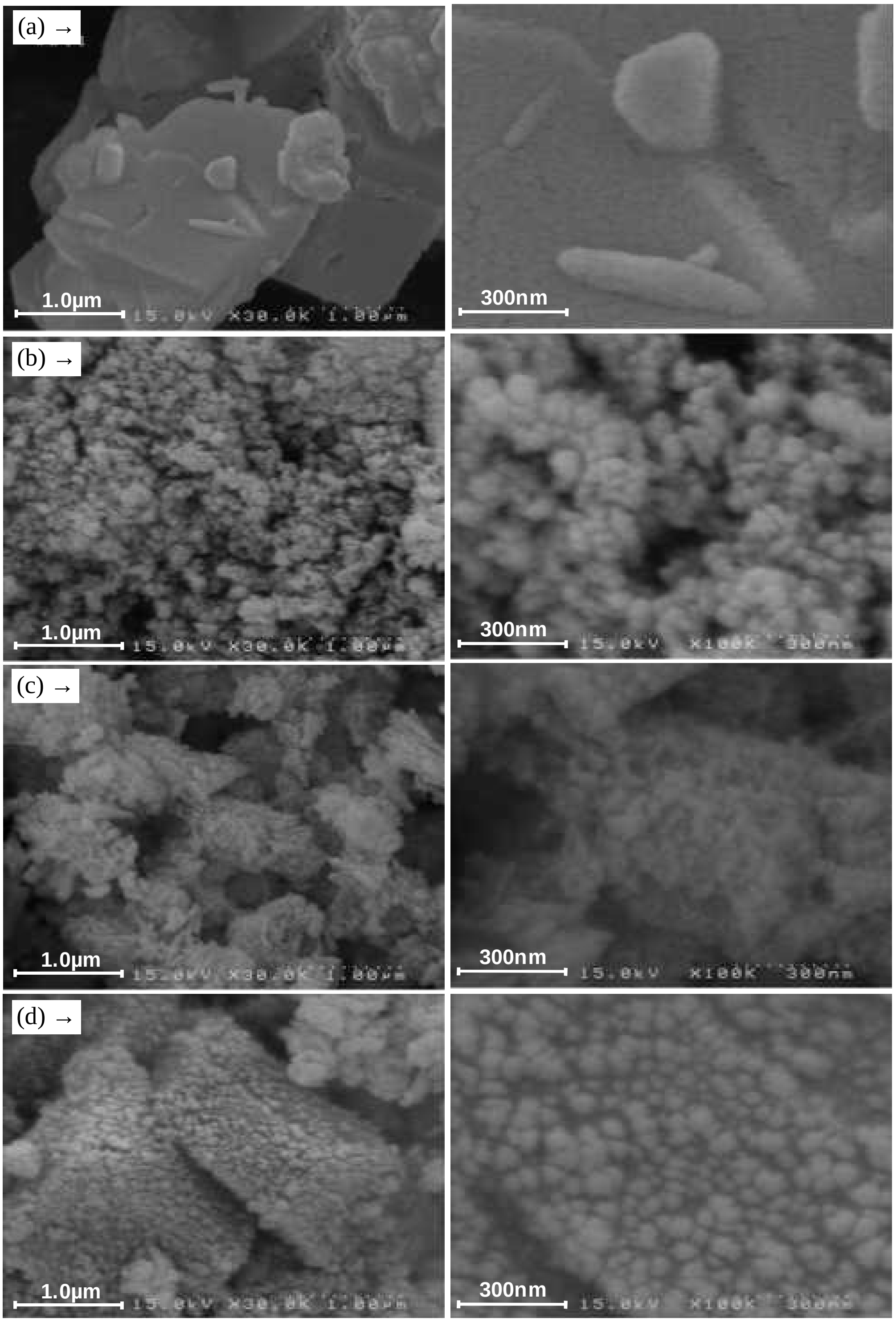

**Fig. 5.** FESEM images of ZSM-5 (a) and synthesized CuO-ZnO-$Al_2O_3$/HZSM-5 nanoparticles via batch co-precipitation (b), semibatch co-precipitation (c) and combined co-precipitation-ultrasound (d) methods.

**Table 1.** Structural properties of CuO-ZnO-$Al_2O_3$/HZSM-5 nanoparticles synthesized via batch co-precipitation, semibatch co-precipitation and combined co-precipitation-ultrasound methods.

| Method | $S_{BET}$ [a] | Crystallite size[a] (nm) | | | Crystallite phase | | |
|---|---|---|---|---|---|---|---|
| | ($m^2$/g) | ZSM-5 | CuO | ZnO | ZSM-5[b] | CuO[c] | ZnO[d] |
| Support | 247 | 21.6 | - | - | Monoclinic | - | - |
| Batch co-precipitation | 128.8 | 20.4 | 21.3 | 36.1 | Monoclinic | Monoclinic | Hexagonal |
| Semibatch co-precipitation | 140.4 | 21.3 | 14.3 | 32.1 | Monoclinic | Monoclinic | Hexagonal |
| Combined Co-precipitation-ultrasound | 109.6 | 19.8 | 7.75 | 29.2 | Monoclinic | Monoclinic | Hexagonal |

a. Crystallite size estimated by Scherre's equation.
b. Reference code (JCPDS): 00-042-0024
c. Reference code (JCPDS): 01-080-1268
d. Reference code (JCPDS): 01-076-0704

Fig. 6 shows the size distribution of the nanoparticles prepared using combined co-precipitation-ultrasound method. The analysis was carried out using ImageJ software. It can be seen that the majority of nanoparticles have a small size around 30-60 nm with narrow size distribution. Using this analysis the mean size distribution of metal oxide phase over HZSM-5 is estimated 48.67 nm.

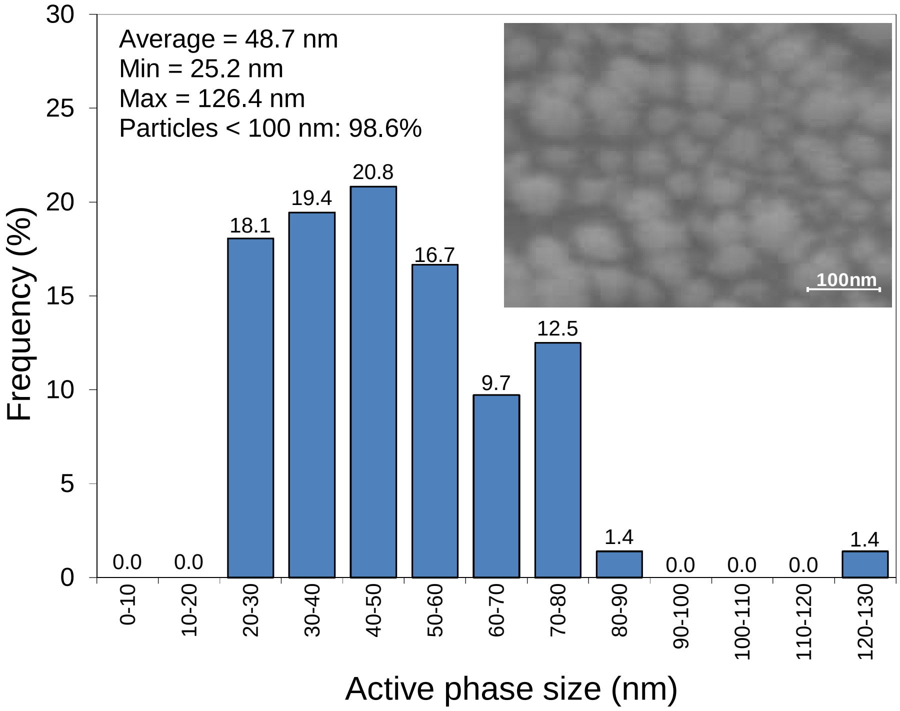

**Fig. 6.** Estimation of active phase size distribution of synthesized CuO-ZnO-$Al_2O_3$/HZSM-5 nanoparticle via combined co-precipitation-ultrasound method using FESEM image.

### 3.3 BET Analysis

Table 1 compares the surface area of synthesized nanoparticle using different preparation methods. The HZSM-5 has shown high surface area of 300 $m^2/g$, however loading of CuO-ZnO-$Al_2O_3$ decreases the specific surface area of synthesized samples in all methods. Results indicated that the surface area of the sample synthesized via semibatch co-precipitation method is 140 $m^2/g$, which is the highest obtained surface area among used methods in this research. In the batch co-precipitation method, the surface area is 129 $m^2/g$ and smallest surface area is obtained when combined co-precipitation-ultrasound method was used (110 $m^2/g$). The lowest value of surface area of the nanoparticle prepared via combined co-precipitation-ultrasound method can be attributed to small particle size of CuO-ZnO-$Al_2O_3$ and strong contact of them to ZSM-5. This can be addressed by plugging the pore structure of ZSM-5 with CuO-ZnO-$Al_2O_3$.

### 3.4 TG-DTG Analysis

Fig. 7 shows TGA-DTG analysis of non-calcined CuO-ZnO-$Al_2O_3$/HZSM-5 nanoparticles synthesized via batch co-precipitation (a), semibatch coprecipitation (b) and combined co-precipitation-ultrasound (d) methods. Furthermore, TGA-DTG analysis of calcined nanoparticle which was synthesized via semibatch copre-cipitation is shown in Fig. 7c. In all methods the decomposition started at 100°C and was completed at 400°C.

In batch and semibatch co-precipitation methods (Fig. 7a and b, respectively) the decomposition of the precursor proceeded in one step. Before decomposition step, the nanoparticles lost 3-5% of their weight between 100 and 150°C due to desorption of physisorbed and chemisorbed water. At decomposition stage, the weight loss took place between 150 and 400°C and precursor lost 12-16% of its weight in this step. It can be attributed to the decomposition of carbonate precursors, so that the decomposition at these high temperature regions produces water and carbon dioxide simultaneously. Since consumption of the sodium carbonate in batch co-precipitation method was higher than semibatch co-precipitation method, the weight loss due to carbonate decomposition in batch co-precipitation was higher than semibatch co-precipitation method.

In combined co-precipitation-ultrasound method (Fig. 7d), there was only one weight loss step between 100 and 150°C. This step can be attributed to the evaporation and removal of the surface adsorbed water. According to the synthesis procedure, in this method firstly CuO-ZnO-$Al_2O_3$ metal oxides were synthesized by co-precipitation method, then sonochemically dispersed over HZSM-5 after calcination at 350°C. Therefore, there were no precursor carbonates in sonochemical treated slurry. This is the reason why there was no decomposition stage for this nanoparticle. TGA analysis shows that carbonates have been decomposed before 350°C, which indicates that this temperature is suitable for calcination of synthesized nanoparticles.

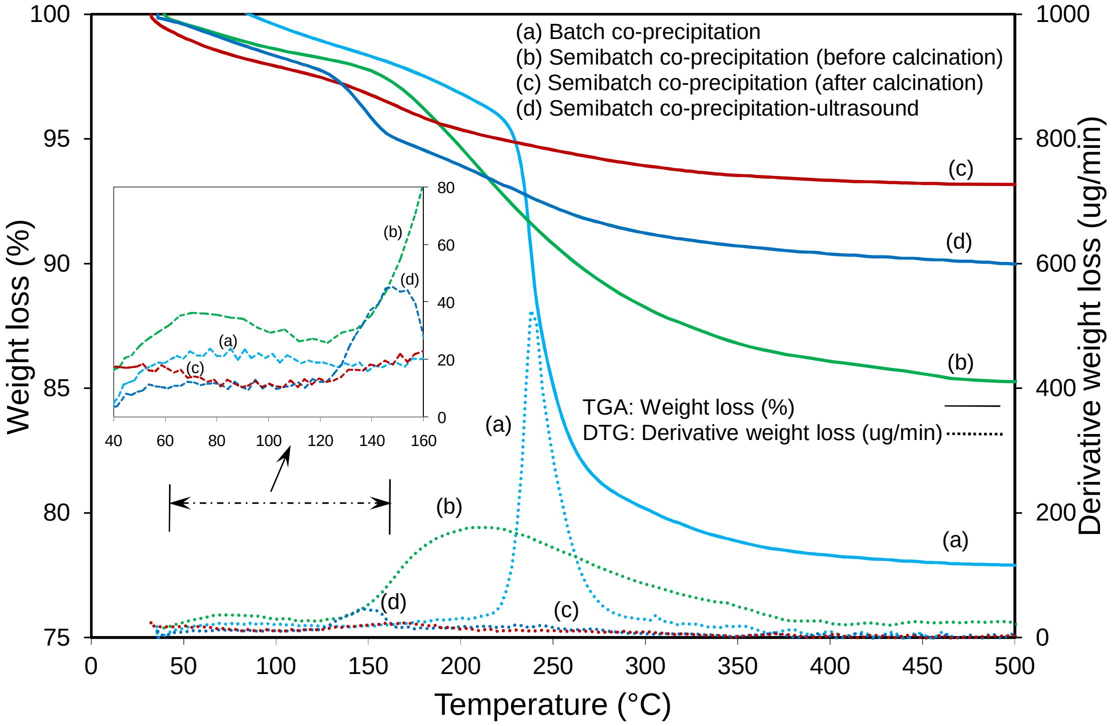

**Fig. 7.** TG-DTG analysis of synthesized CuO-ZnO-$Al_2O_3$/HZSM-5 nanoparticle via batch co-precipitation (a), semibatch co-precipitation (b-c) and combined co-precipitation-ultrasound (d) methods. (a, b, d: before calcinations, c: after calcinations)

### *3.5 FTIR Analysis*

Fig. 8 shows FTIR spectrum of synthesized CuO-ZnO-$Al_2O_3$/HZSM-5 nanoparticles via different methods. As can be seen in Fig. 8, FTIR patterns of synthesized nanoparticles have similar trend in all of methods. Results proved that CuO and ZnO phases were formed and HZSM-5 structure was not damaged during nanocomposite synthesis steps. The FTIR spectrum of HZSM-5 showed bands at 455, 555, 800, 1095 and 1240cm$^{-1}$, which are assigned to different vibrations of tetrahedral and framework atoms in HZSM-5 [38].

The strongest absorption peak at 1095 cm$^{-1}$ is assigned to the framework stretching vibration band of Si(Al)-O in tetrahedral Si(Al)$O_4$ in raw HZSM-5 . The position of this bond remains almost unchanged in all of nanocomposites, indicating that HZSM-5 structure is not destroyed even after it is loaded with CZA nanoparticles. Furthermore, not any characteristic bond was observed for other impurities such as $Cu(OH)_2$ or $Zn(OH)_2$ in FTIR patterns. These results support and complement the XRD data. Furthermore, the broad absorption band at 3450 cm$^{-1}$ was attributed to the hydroxyl groups, which were extensively hydrogen, bonded. The band at ca. 1645 cm$^{-1}$ was assigned to the bonding vibrational mode of the interlayer water molecules [39].

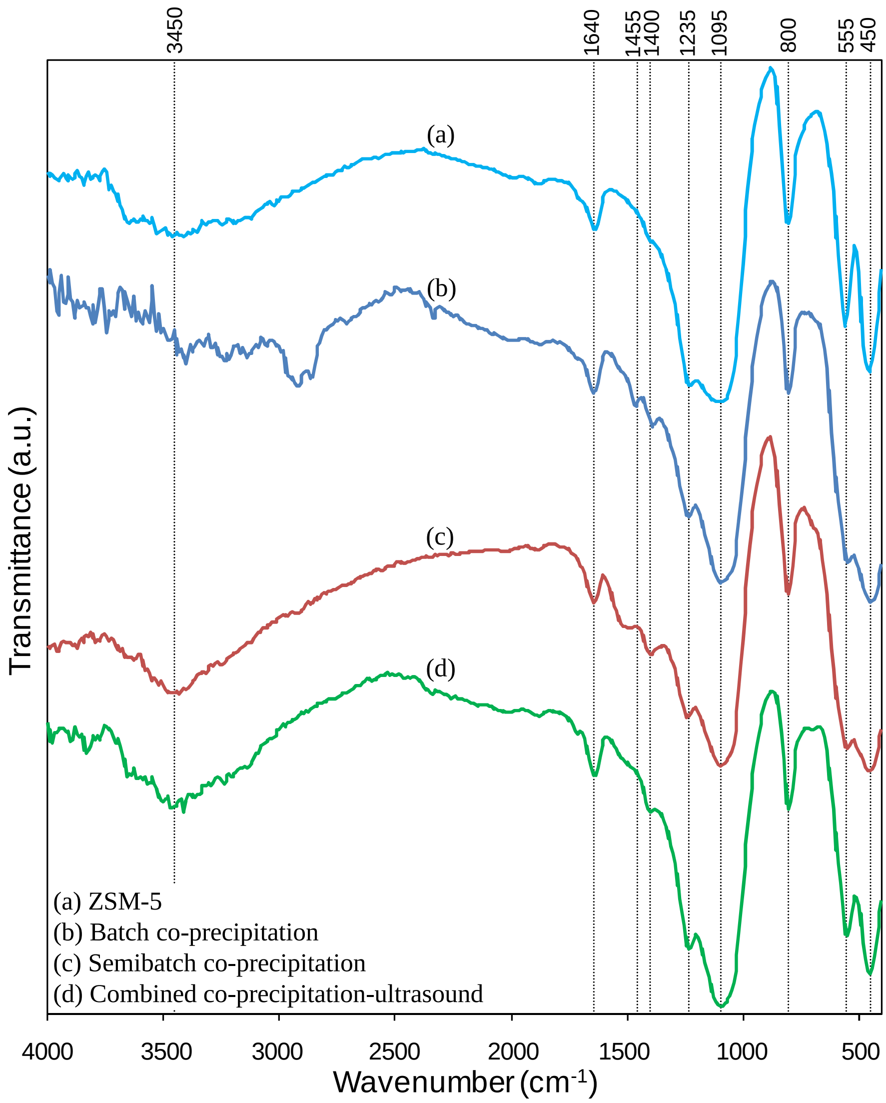

**Fig. 8.** FTIR spectrum of ZSM-5 (a) and synthesized CuO-ZnO-$Al_2O_3$/HZSM-5 nanoparticles via batch co-precipitation (b), semibatch co-precipitation (c) and combined co-precipitation-ultrasound (d) methods.

### *3.6 Reaction Mechanism of CuO-ZnO-$Al_2O_3$ Nanoparticle Formation over HZSM-5*

Fig. 9 shows the effect of calcination process on structural properties of the synthesized nanoparticle via semibatch-co-precipitation method. As can be seen in Fig. 9, after calcinations many bands related to organic materials were eliminated. The IR spectrum of noncalcined sample indicates the presence of carbonate ions. The strong absorption band at 1400 and 1500cm$^{-1}$ originates from the $CO_3^{2-}$ ion. The IR bands observed below 1000 cm$^{-1}$ can be attributed to carbonate and the metal hydroxyl modes (M = Cu, Zn and Al) [40, 41].

As can be seen in Fig. 7b, there is a major weight loss step in non-calcined sample. It may be due to decomposition of carbonate to $CO_2$ and $H_2O$. However, in calcined sample (Fig. 7c) there is only one weight loss step of water desorption between 100-200°C. This result is confirmed by FTIR analysis (Fig. 9)

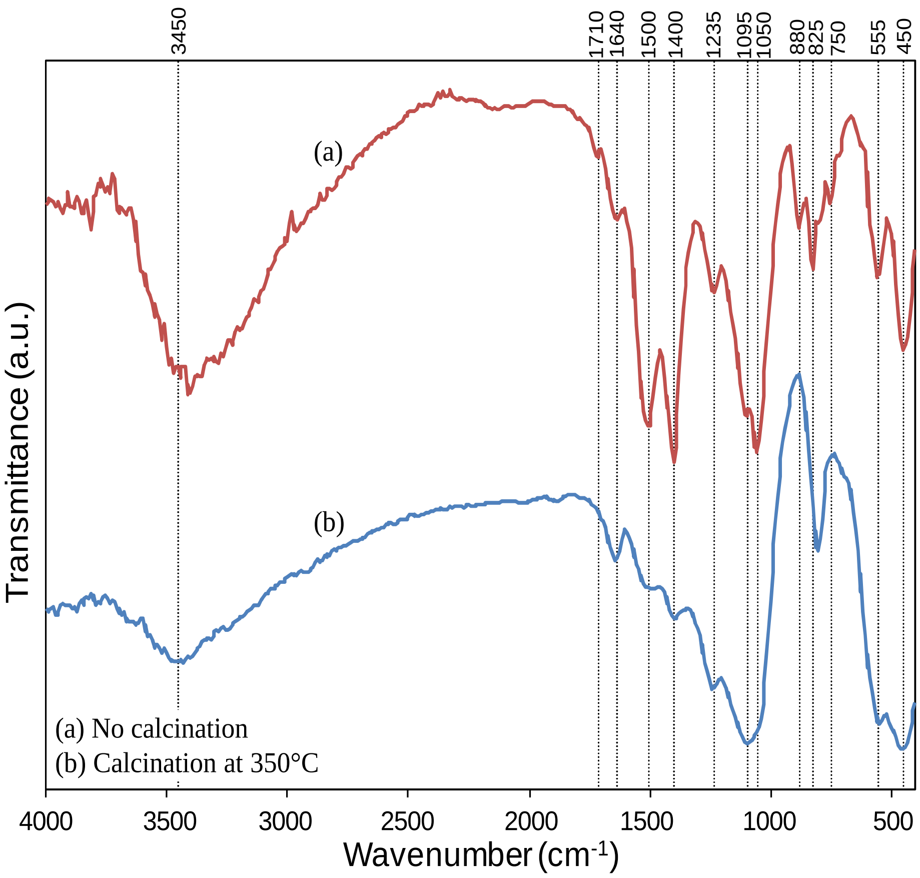

**Fig. 9.** FTIR spectrum of synthesized CuO-ZnO-$Al_2O_3$/HZSM-5 nanoparticle via semibatch co-precipitation method before (a) and after calcination (b) at 350°C.

According to the results of FTIR and TG-DTG analysis, the mechanism of the formation of CuO-ZnO-$Al_2O_3$ nanoparticle over HZSM-5 is suggested by reactions steps of (1)-(4) and reaction network shown in Fig. 10. As can be noted, the process composed of four steps. Firstly, sodium carbonate was hydrolyzed and sodium hydroxide and carbonic acid was obtained. Then $CO_3^{2-}$ was formed from decomposition of carbonic acid according to reaction (2). In the metal nitrate solution, the positive ions are copper (Cu), zinc (Zn) and aluminum (Al) while the nitrate ($NO_3^-$) is the negative ion. It can be noted that in the sodium hydroxide solution, the sodium (Na) is the positive ion and the (OH) is the negative ion. When metal nitrate solution and sodium hydroxide was mixed, an ion exchange was carried out and the metal and sodium ions were exchanged in the compounds. One of the products formed after this ion exchange are metal hydroxides $Cu(OH)_2$ ,$Zn(OH)_2$ and $Al(OH)_3$ which are in-soluble, green gelatin-like solid and was precipitated on HZSM-5 to form [CuZn-$Al_2(OH)_{10}$] HZSM-5 $(CO_3)_5$ $(H_2O)_n$. The other products are soluble in water and remain in the liquid phase. Finally, nanosized CuO-ZnO-$Al_2O_3$ /HZ-SM-5 was synthesized after the calcination of [$CuZnAl_2(OH)_{10}$]HZSM-5$(CO_3)_5$ $(H_2O)_n$].

$$Na_2CO_3 + H_2O \longrightarrow 2\ NaOH\ (aq) + H_2CO_3 \qquad (2)$$

$$H_2CO_3 \longrightarrow 2H^+ + CO_3^{2-} \qquad (3)$$

$$\begin{aligned} &Cu(NO_3)_2 + Zn(NO_3)_2 + 2Al(NO_3)_3 + HZSM\text{-}5 + 10NaOH + 5CO_3^{-2} + nH_2O \longrightarrow \\ &[CuZnAl_2(OH)_{10}]HZSM\text{-}5\,(CO_3)_5\,(H_2O)_n + 10NaNO_3 \end{aligned} \qquad (3)$$

$$[CuZnAl_2(OH)_{10}]HZSM\text{-}5\,(CO_3)_5\,(H_2O)_n \longrightarrow [CuO\text{-}ZnO\text{-}Al_2O_3]HZSM\text{-}5 + 5CO_2 + nH_2O \qquad (4)$$

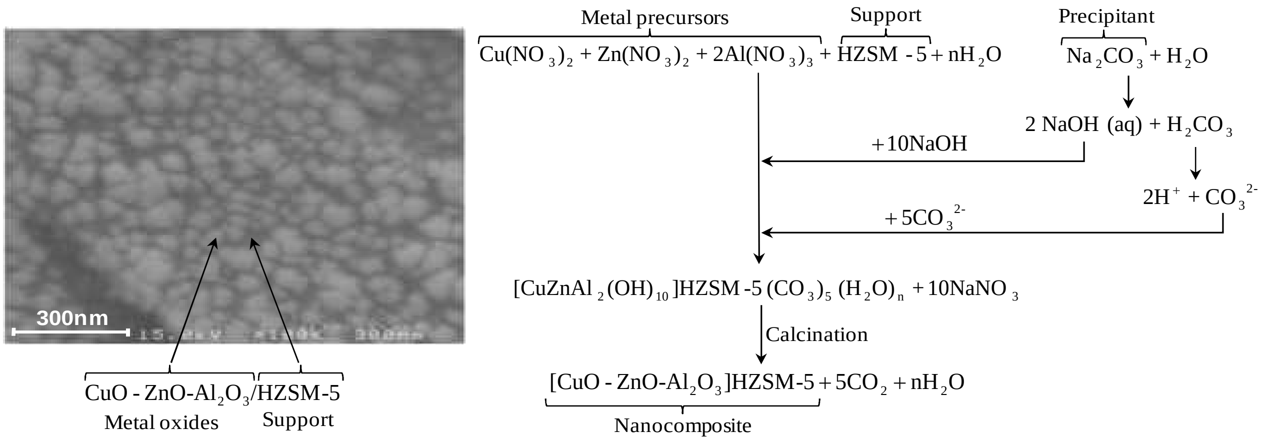

**Fig. 10.** Reaction mechanism of formation of CuO-ZnO-$Al_2O_3$ nanoparticle over HZSM-5 synthesized via semibatch co-precipitation method.

## 4. CONCLUSION

CuO-ZnO-$Al_2O_3$/ZSM-5 nanoparticle was prepared employing batch co-precipitation, semibatch co-precipitation and combined semibatch co-precipitation-ultrasound methods followed by calcination at 350°C for 5 hr successfully. XRD patterns and FTIR analysis were addressed the formation of CuO-ZnO-$Al_2O_3$ nanoparticle over HZSM-5. Results indicated that the ultrasound energy affected the physic-chemical features of synthesized nanoparticles. Therefore, the sample prepared by this method has favorable characteristics such as small grain size and small crystallite size. A possible pathway of precipitation process is proposed based on the FTIR and TGA analysis. TGA-DTG analysis showed that 350°C was a suitable temperature for calcinations of synthesized nanoparticles. Further investigations of the other preparation methods for synthesis of nanoparticle are currently underway.

## Acknowledgements

The authors gratefully acknowledge Sahand University of Technology for the financial support of the project as well as Tabriz Refinery Company and Iran Nanotechnology Initiative Council for complementary financial support.

## REFERENCES

[1] C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, *Chem. Rev.*, 105, 1025 (**2005**).

[2] A. B. Djurisic, A. M. C. Ng, X. Y. Chen, *PQE*, 34, 191 (**2010**).

[3] Q. Qi, T. Zhang, Y. Zeng, H. Yang, *Sensor Actuat. B-Chem.*, 137, 21 (**2009**).

[4] G. N. S. Vijayakumar, S. Devashankar, M. Rathnakumari, P. Sureshkumar, *J. Alloys Compd.*, 507, 225 (**2010**).

[5] K.-S. Lin, S. Chowdhury, H.-P. Yeh, W.-T. Hong, C.-T. Yeh, *Catal. Today*, 164, 251 (**2011**).

[6] C.-C. Chang, C.-T. Chang, S.-J. Chiang, B.-J. Liaw, Y.-Z. Chen, *Int. J. Hydrogen. Energ.*, 35, 7675 (**2010**).

[7] C. Yaqing, L. Xiaonian, L. Huazhang, *Chem. Eng. Sci.*, 61, 1540 (**2006**).

[8] H. Ma, P.L. Williams, S.A. Diamond, *Environ Pollut.*, 172, 76 (**2013**).

[9] T. Ates, C. Tatar, F. Yakuphanoglu, *Sensor Actuat. A-Phys.*, 190, 153 (**2013**).

[10] J.-H. Kim, M.J. Park, S.J. Kim, O.-S. Joo, K.-D. Jung, *Appl. Catal., A*, 264, 37 (**2004**).

[11] D. Mao, J. Xia, B. Zhang, G. Lu, *Energy Convers. Manage*., 51, 1134 (**2010**).

[12] Y. Zhao, J. Chen, J. Zhang, *J. Nat. Gas Chem.*, 16, 389 (**2007**).

[13] J. Abu-Dahrieh, D. Rooney, A. Goguet, Y. Saih, *Chem. Eng. J.*, 203, 201 (**2012**).

[14] C.-C. Chang, C.-C. Hsu, C.-T. Chang, Y.-P. Chen, B.-J. Liaw, Y.-Z. Chen, *Int. J. Hydrogen. Energ.*, 37, 11176 (**2012**).

[15] C.-C. Chang, J.-W. Wang, C.-T. Chang, B.-J. Liaw, Y.-Z. Chen, *Chem. Eng. J.*, 192, 350 (**2012**).

[16] P. S. Sai Prasad, J. W. Bae, S.-H. Kang, Y.-J. Lee, K.-W. Jun, *Fuel Process. Technol.*, 89, 1281 (**2008**).

[17] F. S. Ramos, A. M. D. D. Farias, L. E. P. Borges, J. L. Monteiro, M. A. Fraga, E. F. Sousa-Aguiar, L. G. Appel, *Catal. Today*, 101, 39 (**2005**).

[18] L. Zhang, Y. Zhang, S. Chen, *Appl. Catal., A*, 415–416, 118 (**2012**).

[19] M.-R. Yu, G. Suyambrakasam, R.-J. Wu, M. Chavali, *Mater. Res. Bul.*, 47, 1713 (**2012**).

[20] E. Samei, M. Taghizadeh, M. Bahmani, *Fuel Process. Technol.*, 96, 128 (**2012**).

[21] X. Li, H. Liu, J. Wang, H. Cui, X. Zhang, F. Han, *Mater. Sci. Eng*., A, 379, 347 (**2004**).

[22] R. Khoshbin, M. Haghighi, N. Asgari, *Mater. Res. Bul.*, 48, 767 (**2013**).

[23] R. Khoshbin, M. Haghighi, *J. Nanosci. Nanotech.*, 13, 4996 (**2013**).

[24] R. Khoshbin, M. Haghighi, *Chem. Eng. Res. Des.*, 91, 1111 (**2013**).

[25] J. Li, Y. Pan, F. Qiu, Y. Wu, J. Guo, *Ceram. Int.*, 34, 141 (**2008**).

[26] R. Khoshbin, M. Haghighi, *Chin. J. Inorg. Chem.*, 28, 1967 (**2012**).

[27] N. Rakmak, W. Wiyaratn, C. Bunyakan, J. Chungsiriporn, *Chem. Eng. J.*, 162, 84 (**2010**).

[28] A. R. Abbasi, A. Morsali, *Ultrason. Sonochem.*, 17, 704 (**2010**).

[29] R. R. Ramos, C. Bolivar, J. Castillo, J. Hung, C. E. Scott, *Catal. Today*, 133-135, 277 (**2008**).

[30] M. Amin Alavi, A. Morsali, *J. Exp. Nanosci*., 5, 93 (**2010**).

[31] A. Askarinejad, M. Bagherzadeh, A. Morsali, *J. Exp. Nanosci.*, 6, 217-225 (**2011**).

[32] H. Li, J. Zhang, H. Li, *Catal. Commun.*, 8, 2212 (**2007**).

[33] C. Pirola, C.L. Bianchi, A. Di Michele, P. Diodati, D. Boffito, V. Ragaini, Ultrason. Sonochem., 17, 610 (**2010**).

[34] V. Sáez, T. J. Mason, Molecules, 14, 4284 (**2009**).

[35] J. K. Kim, F. Martinez, I. S. Metcalfe, *Catal. Today*, 124, 224 (**2007**).

[36] X. Zhang, L. Zhong, Q. Guo, H. Fan, H. Zheng, K. Xie, *Fuel*, 89, 1348 (**2010**).

[37] R. T. Figueiredo, A. Martinez-Arias, M. L. P. Granados, J. L. G. Fierro, *J. Catal*., 178, 146 (**1998**).

[38] I. Othman Ali, *Mater. Sci. Eng.*, A, 459, 294 (**2007**).

[39] L. Chen, L. Li, G. Li, *J. Alloys Compd.*, 464, 532 (**2008**).

[40] L. Zhang, W. Lu, Y. Feng, J. Ni, Y. Lü, X. Shang, *Acta Physico-Chimica Sinica*, 24, 2257 (**2008**).

[41] W. Sun, W.-l. Liu, Y.-h. Hu, J. Cent. *South Univ. Tech.*, 15, 373 (**2008**).

# مطالعه مقایسه‌ای توزیع نانو ذرات $CuO\text{-}ZnO\text{-}Al_2O_3$ بر روی HZSM-5 از طریق روش‌های هم رسوبی پیمانه‌ای، هم رسوبی شبه پیمانه‌ای و هم رسوبی- فراصوت ترکیبی

**ر. خوشبین، م. حقیقی[*]**

دانشجوی دکتری و دانشیار دانشکده مهندسی شیمی، مرکز تحقیقات رآکتور و کاتالیست دانشگاه صنعتی سهند،
شهر جدید سهند، تبریز، ایران

(تاریخ دریافت: خرداد ۱۳۹۲ - تاریخ پذیرش: مرداد ۱۳۹۲)

## چکیده:

یک سری نانو ذرات $CuO\text{-}ZnO\text{-}Al_2O_3$ بر روی HZSM-5 با موفقیت با روش های مختلف هم رسوبی پیمانه‌ای، هم رسوبی شبه پیمانه‌ای و هم رسوبی- فراصوت ترکیبی تهیه شد. نیترات های مس، روی و آلومینیوم به عنوان پیش ماده سنتز استفاده گردید، در حالیکه Na-ZSM-5 به عنوان بستر کامپوزیت و سدیم کربنات به عنوان عامل رسوب دهنده بکار گرفته شد. اثرات روش های تهیه روی خواص فیزیکی شیمیایی نانو ذرات سنتز شده توسط تکنیک های XRD، BET، FESEM، FTIR و TGA-DTG مطالعه شد. بعلاوه مکانیسم تشکیل $CuO\text{-}ZnO\text{-}Al_2O_3$ بر روی HZSM-5 پیشنهاد شد. تشکیل $CuO\text{-}ZnO\text{-}Al_2O_3$ بر روی HZSM-5 با اندازه ذرات همگن بعد از کلسینه شدن در دمای 350°C به مدت ۵ ساعت ارایه شد. نتایج بدست آمده نشان می دهند که ساختار بلور، رفتار وزن سنج حرارتی و مورفولوژی سطح نانو کامپوزیت به شدت به روش های تهیه وابسته می باشد. روش هم رسوبی- فراصوت ترکیبی در کنترل اندازه بلور و توزیع $CuO\text{-}ZnO\text{-}Al_2O_3$ برتری دارد. نتیجه این روش ایجاد ذرات بلور خیلی ریز با شکل کروی و توزیع اندازه ذرات ریز می باشد.

---

[*] مولف مسئول: *haghighi@sut.ac.ir*