

ZSM-5 Zeolite As Host Material for Semiconductor Nanoparticles

A. Pourahmad^{1*}, Sh. Sohrabnezhad²

1. Department of Chemistry, Faculty of Science, Islamic Azad University, Rasht Branch, I.R. Iran
2. Department of Chemistry, Faculty of Science, University of Mohaghegh Ardabili, Ardabil, I.R. Iran

(*) Corresponding author: pourahmad@iaurasht.ac.ir

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Abstract:

This work describes the optical and structure properties of nickel sulfide and cobalt sulfide nanoparticles in ZSM-5 zeolite. The samples were obtained by sulfidation of the Ni²⁺ and Co²⁺ ion-exchange ZSM-5 zeolites in a Na₂S solution at room temperature. The optical properties of the samples were studied by UV-visible spectroscopy. Their crystalline structure and morphology were studied by X-ray diffraction and scanning electron microscopy. Specific surface area and infrared spectroscopy results reveal that nanoparticles could grow on the surface area of ZSM-5 zeolites. Absorption peaks at higher energy than the fundamental adsorption edge of bulk nickel sulfide and cobalt sulfide indicate quantum confinement effect in nanoparticles as a consequence of their small size. The absorption spectra show that the optical band gap varies in the range of 3.91-4.72 eV.

Keywords: Nanocomposites; Nanostructures; ZSM-5 zeolite; X-ray diffraction; Semiconductors; Infrared spectroscopy

1- INTRODUCTION

Transition metal sulfides, in particular, exhibit variable and novel optical and electrical properties, and some of them are used for the fabrication of devices [1]. They are also envisioned for a number of exciting applications including catalysts, heavy metal sponges-absorbents, chemical sensors, luminescent devices, and even superconductors [2,3]. Because of the wide applications mentioned above, highly crystalline particles with almost mono-disperse size distribution and regular morphology are required. It is well known that transition metal sulfide, such as NiS, ZnS, CoS and CdS, etc., have been prepared by various methods in the past few decades [4,5]. The same synthesis strategy can also be used to obtain transition metal sulfide nanoparticles.

Many different methods have been used for

preparation of semiconductor nanoparticles, e.g. preparation of nanoparticles in solution [6], glasses [7] or polymers [8]. However, it is not easy to control the size distribution of small particles with countable number of atoms in this method. The regular pore structure of microporous materials MFI-type zeolite could offer a suitable reaction chamber for the controlled assembly of nanostructure materials. Indeed, MFI-type (ZSM-5) zeolite with 10-membered oxygen rings having uniform pore structure can comfortably trap the guest molecules in the micropores. Due to the well-defined pore size, high surface area associated with the open framework, microporous solids loaded with nanoscale particles within their pores have received considerable attention in recent years, especially in preparing semiconductor nanoparticles, but most of microporous materials used as host need a modification procedure to functionalize the

micropore internal surface [9,10].

In these works, an ion exchange technique was used. Nanoparticles with a broad size distribution were formed on the external surface, and changes in the zeolite framework were observed. Here, the growth of NiS and CoS nanoparticles in obtained ZSM-5 zeolite host by Ni or Co ion exchange followed by treatments in Na₂S solution is studied.

2. EXPERIMENTAL

The ZSM-5 zeolite was synthesized in our laboratory based on the described procedure in the literature [11]. The unit cell composition of zeolite, calculated from our obtained EDX data, was Na_{0.3}TEA_{3.2}[Al_{3.5}Si_{92.5}O₁₉₂]. 10H₂O. As precursors of NiS and CoS semiconductors, two solutions of NiSO₄ and CoSO₄ (0.1 M) were prepared. To 50 ml of NiSO₄ and CoSO₄ solutions, 1 g of ZSM-5 powder was separately added and stirred for 32 h at 25°C. The samples were then washed to remove nonexchanged Co²⁺ and Ni²⁺ and air-dried. Sulfidation of the Co²⁺ and Ni²⁺ ion exchanged zeolites were carried out with 0.1 M Na₂S solution. To make the reaction with the S²⁻ ion, one g of Ni²⁺ or Co²⁺ - exchanged zeolite was added to 50 mL of 0.1 M solution of Na₂S at 25°C and magnetically stirred for 2 h. The samples were washed with deionized water and collected by filtration. The obtained samples were fine powders in jasper green and white green colors for CoS-ZSM-5 and NiS-ZSM-5 respectively. They were stable at the ambient conditions.

In this work, the bulk NiS and CoS were prepared in the conventional precipitation method by adding 0.1 M of Na₂S solution to the stirred equimolar amount of NiSO₄ and CoSO₄ solutions (0.1M). The resulting bulk precipitated products were then repeatedly washed with distilled water until free from S²⁻ ions, dried in an air-oven and calcined at 500°C for 6 h. The samples were dark color fine powders.

Powder X-ray diffraction patterns of the samples were recorded using a Philips X, Pert diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). UV-Vis absorption spectra were recorded using a shimadzu 1600 PC

in the spectral range of 190-900 nm. The specific surface area and pore volume of the samples were measured using a Sibata Surface Area Apparatus 1100. All of the samples were first degassed at 250°C for 2 h. Chemical analysis of the samples was done by energy dispersive X-ray analysis (EDX) joined to a LEO 1430 VP scanning electron microscopes. Infrared spectra on KBr pellet were measured on a Bruker spectrophotometer.

3. RESULTS AND DISCUSSION

The powder XRD results of the ZSM-5 zeolite and the host-guest composite materials, CoS-ZSM-5, NiS-ZSM-5 (Figure 1) show similar diffraction peaks indicative of ZSM-5 zeolite. But, some differences, such as the broadening of the diffraction peaks, increasing or decreasing of some peaks intensity as well as the shift to the peak position to the slightly lower angles can be observed in the spectra. In fact, the intensities of the more peaks in the host-guest nanocomposite materials are decreased with respect to XRD pattern ZSM-5 zeolite. This difference of the peak intensities, in agreement with the reported results for other zeolites [12,13] can be related to the presence or incorporation of semiconductors in the matrix structure. In the present patterns there is an increase and a decrease in some peaks intensity when the CoS particles are present in the ZSM-5 zeolite. These peaks are located approximately at 2θ equal 29° and 46° which are due to the reflection of the (100), (102) planes, in the CoS phase [4]. Proceeding in the same way, we found a decrease in intensity of some peaks in the case of NiS at $2\theta = 46^\circ\text{-}50^\circ$ which are related to the (102), (131) and (410) planes of NiS phase [14].

The value of average particles size calculated by Scherer equation, for the lines at $2\theta=29^\circ, 49^\circ$ of CoS-ZSM-5 and $2\theta=46^\circ\text{-}50^\circ$ for NiS-ZSM-5 nanoparticle were 6 and 4 nm respectively.

To investigate the locations of the guest materials in the composite materials, we measured the specific surface area and pore volumes of the ZSM-5 composite materials.

The results of the specific surface area and pore volume measurements for ZSM-5, NiS-ZSM-5 and CoS-ZSM-5 (Table 1), show that the pore volumes of the host zeolite, which was 0.12 ml g^{-1} for ZSM-5 zeolite no change for the NiS-ZSM-5 and CoS-ZSM-5 composite materials respectively. The specific surface areas of the composite materials change from $300 \text{ m}^2\text{g}^{-1}$ for ZSM-5 to 298 and $340 \text{ m}^2\text{g}^{-1}$ for CoS-ZSM-5 and NiS-ZSM-5 respectively. In the previous work, it was shown that NiS and CoS was located in the channels of mordenite zeolite [15]. In CoS-Mordenite and NiS-Mordenite nanocomposite decreasing of the pore volumes nanoparticles in mordenite zeolite were more ($46.4 \text{ m}^2\text{g}^{-1}$) than CoS and NiS in ZSM-5 zeolite. No changes in the pore volume of CoS/NiS ZSM-5 zeolite demonstrate that the guests may be are located on the surface area of ZSM-5 zeolite. On the other hand, The SEM pictures of unloaded ZSM-5 zeolite and the prepared composite show that (Figure 2), CoS and NiS nanoparticles are located outside of ZSM-5 zeolite and this is other document that nanoparticles could grow on the surface area. The crystallites of the unloaded ZSM-5 zeolite, with size $2 \mu\text{m}$, have a very well defined lath shape crystals. The images of the CoS-ZSM-5 and NiS-ZSM-5 composites, show that the lath shape of the ZSM-5 zeolite is not affected by the NiS and CoS loading.

UV-Visible absorption spectra for bulk CoS and NiS nanoparticles prepared from ZSM-5 zeolite matrices is shown in Figure 3. By comparing the adsorption edge of CoS and NiS bulk with CoSZSM-5 and NiSZSM-5 samples it can be seen that a blue shift in the onset of adsorption is observed in mordenite samples. The phenomenon of blue shift of adsorption edge has been ascribed to a decrease in particle size. It is well known that in case of semiconductors the band gap between the valence and conduction band increases as the size of the particle decreases in the nanosize range. This results in a shift in the adsorption edge to a lower wavelength region. The magnitude of the shift depends on the particle size of the semiconductor. In the present study, the NiSZSM-5 sample showed a blue shift compared to the bulk

particles and CoSZSM-5. From the onset of the adsorption edge, the band gap of the nanoparticles was calculated using the method of Tandon and Gupta [16]. From table 1, it can be found that the band gap increase in the order NiSZSM-5>NiS bulk and CoSZSM-5>CoS bulk. These results confirm the presence of NiS and CoS particles on the surface area of ZSM-5 zeolite that could show quantum confinement effects. These band gaps are approximately similar to those observed in the composite material CoSY and NiSY in reference [15].

The IR spectra of ZSM-5, CoSZSM-5 and NiSZSM-5 samples at the range $800\text{-}4000 \text{ cm}^{-1}$ are shown in Figure 4. The IR spectrum of ZSM-5 shows bands at $814, 905, 1165.4$ and 1722 cm^{-1} which are assigned to different vibrations of tetrahedral and framework atoms in ZSM-5 zeolite [17,18]. The spectrum of OH-groups in the parent ZSM-5 shows bands at $3730, 3690$ and 3417 cm^{-1} belong to isolated Si-OH, nano-framework Al and acidic bridged hydroxyls respectively [19].

In the present work, all bands in CoSZSM-5 and NiSZSM-5 samples show a shift to the lower and higher wave numbers with respect to the ZSM-5 zeolite respectively. This shift reveals that nanoparticles could incorporate in ZSM-5 zeolite. The increased intensity is observed in both nanoparticles samples with respect to ZSM-5 zeolite. This increase is related to the extent of perturbation of T-O-T vibrations of the zeolite lattice (bands $1700\text{-}800 \text{ cm}^{-1}$) and the increase acidic bridged hydroxyls vibrations (3417 cm^{-1} band) [20]. Meanwhile, the existence of the bands at 3730 and 3690 cm^{-1} in ZSM-5 implies the decrease in intensity of the nanoparticles samples since SiO_2/Al ratio (aluminum loss) in order to replacing non-framework Al by the corresponding of the metal ion increase. The reaction of ZSM-5 zeolite with cobalt sulfate and nickel sulfate solution replace non-framework Al by Co cation. As a result, significant decrease was observed in intensity of these bands (free Si-OH and non-framework Al). This kind of differences related to the present of CoS/NiS nanoparticles in zeolite.

Table 1: Band gap, specific surface area (BET), pore volume and absorption edge of CoSZSM-5 and NiSZSM-5 samples prepared from zeolite and bulk CoS sample.

| Sample | Band gap (eV) | Specific surface area (m ² /g) | Particle size (nm) | Pore volume (mL/g) | Adsorption edge (nm) |
|-----------------|---------------|---|--------------------|--------------------|----------------------|
| ZSM-5 | | 300 | | 0.12 | |
| CoSZSM-5 | 4.1 | 298 | 6 | 0.11 | 305 |
| NiSZSM-5 | 4.72 | 305 | 4 | 0.12 | 265 |
| CoS bulk | 3.91 | 14 | 18 | 0.038 | 320 |
| NiS bulk | 4.17 | 20 | 10 | 0.042 | 300 |

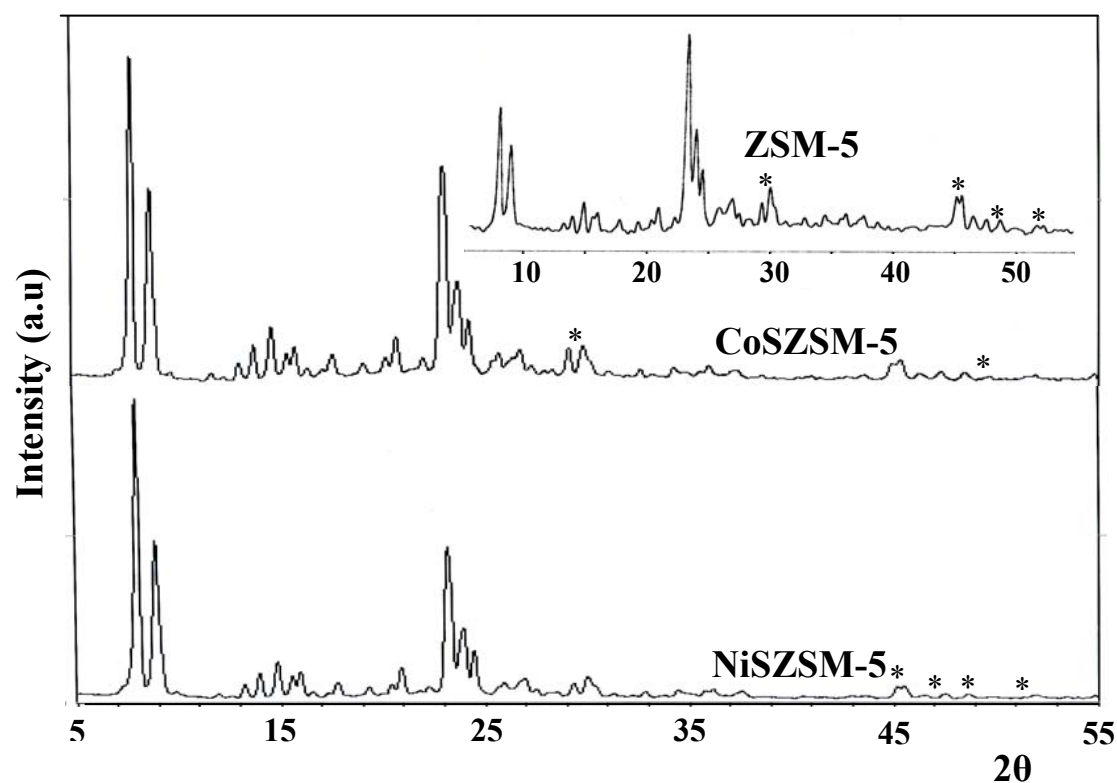


Figure 1: X-ray diffraction patterns of the synthesized ZSM-5 and CoS/NiS nanoparticle samples.

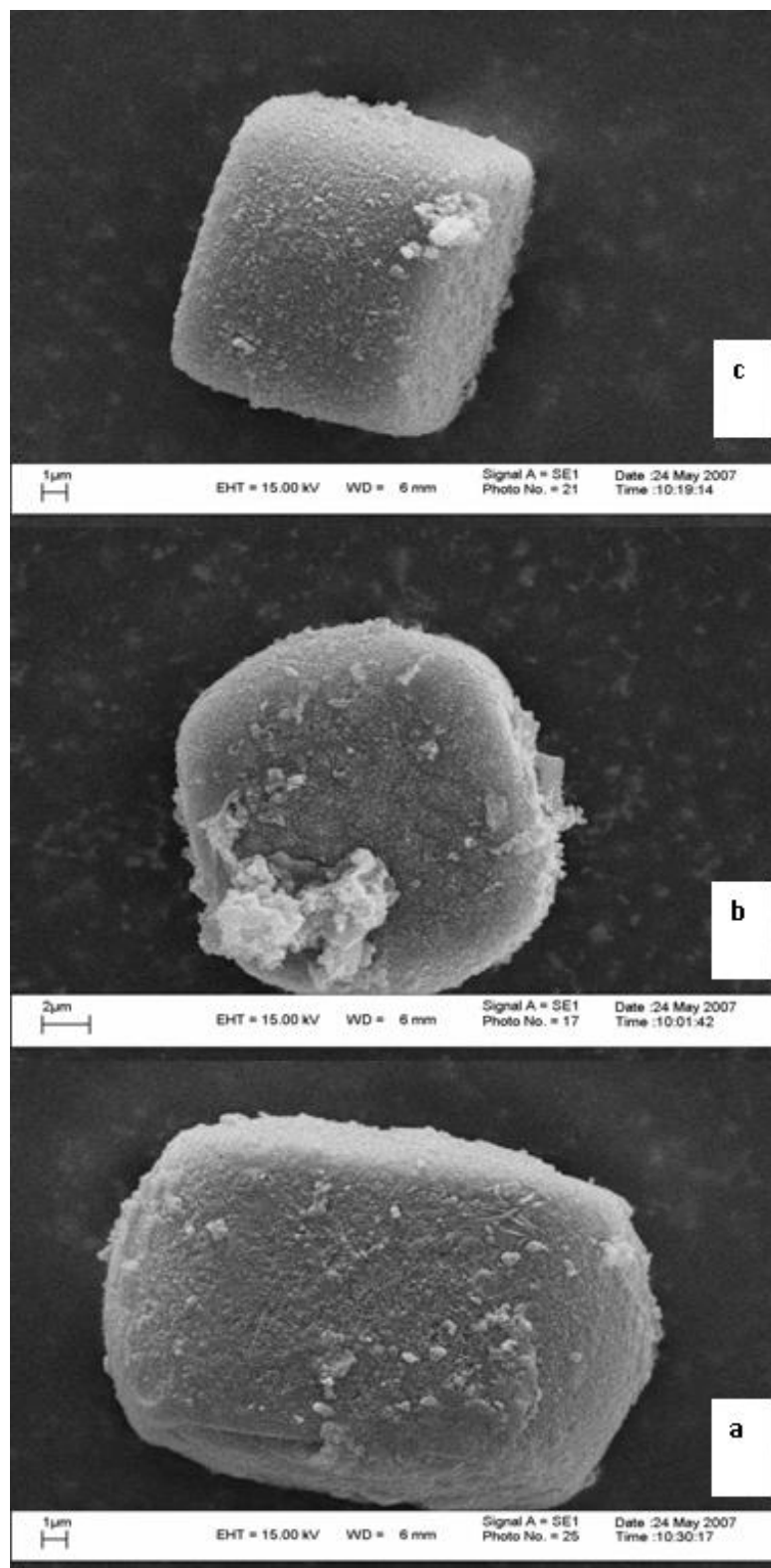


Figure 2: Scanning electron micrograph of (a) ZSM-5 (b) CoSZSM-5 (c) NiSZSM-5.

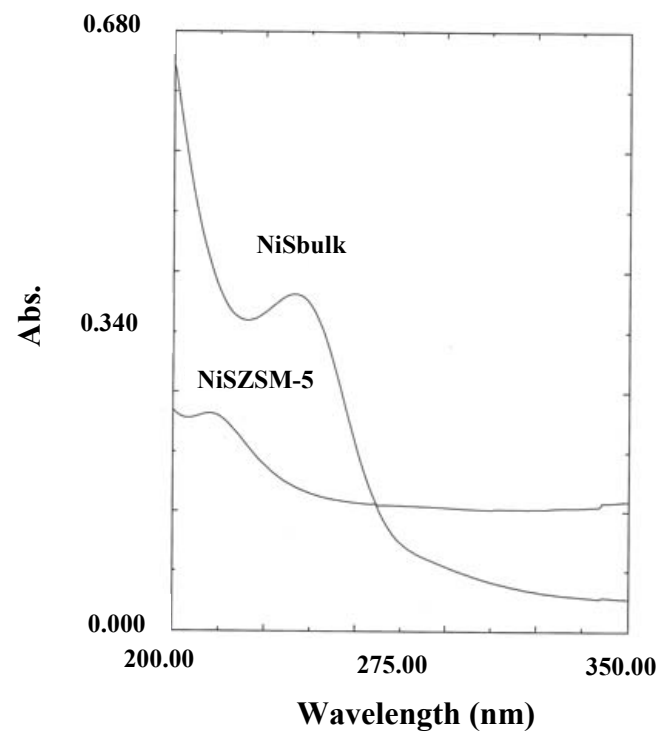
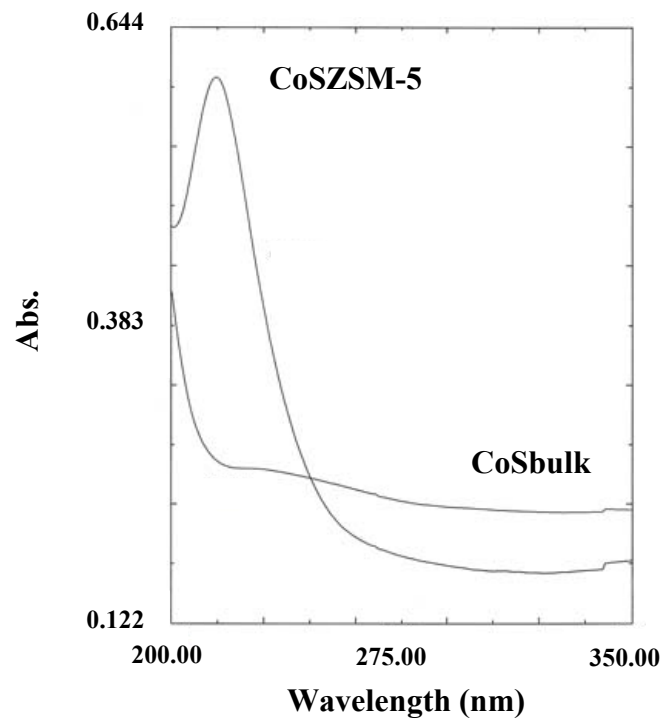


Figure 3: Absorption spectra for the set of CoS/NiS samples.

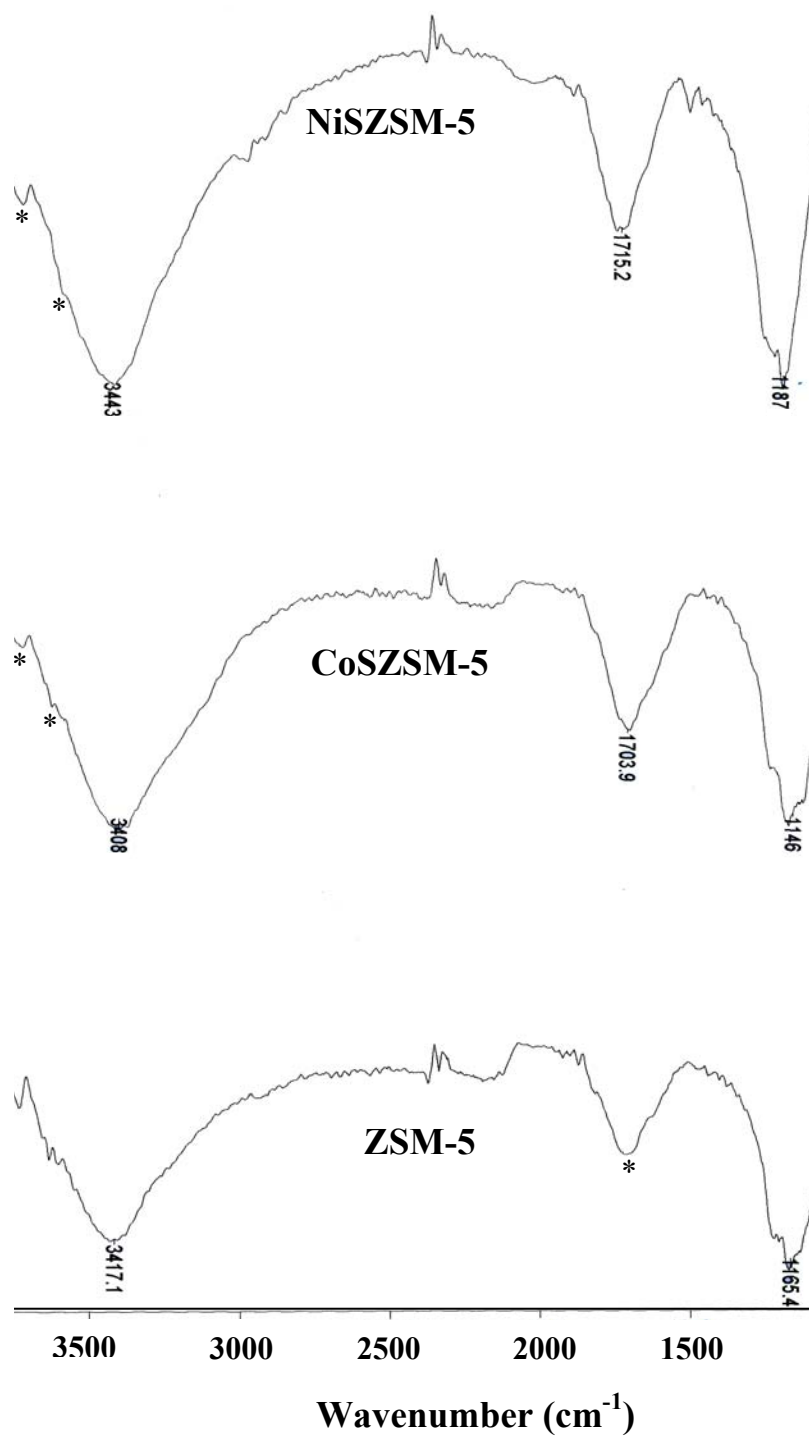


Figure 4: IR spectra of ZSM-5 and CoS/NiS nanoparticles zeolite.

4. CONCLUSIONS

In this paper, ZSM-5 was synthesized and characterized as well crystallized zeolite forming lath shape of the zeolite crystals. The growth of nanoparticles of NiS and CoS was performed by ion exchange of ZSM-5 zeolite in a solution of Co^{2+} or Ni^{2+} ions, followed by treatment of exchanged samples in Na_2S solution. The obtained results show the formation of nanoparticles inside (or on the surface of the matrix) the matrix. The samples exhibit blue shifts in the adsorption edges with respect to the bulk samples. In spite of some changes which were appreciated in the zeolite framework, powder XRD results reflect that the zeolite structure is essentially maintained and the average size of the nanoparticles is 4-6 nm in the ZSM-5 zeolite.

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