

## Incorporation of CoS Nanoparticles into ZSM-5 Zeolite by Hydrothermal and Ion Exchange Methods

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Cobalt sulfide nanoparticles were introduced into the medium-pore zeolite ZSM-5 (Zeolite Scony Mobil Five) by ion exchange in aqueous suspension and also by the addition of cobalt sulfate to the synthesis gel in hydrothermal zeolite synthesis. The latter method was systematically studied in the presence of tetraethylammonium ions as organic agents. The materials were characterized by chemical analysis, x-ray diffraction (XRD), scanning electron microscopy (SEM), Transmission electron microscopy (TEM), energy dispersion x-ray (EDX), IR, BET and diffuse reflectance spectroscopy (DRS). SEM picture and BET were used to discriminate between CoS nanoparticles in the zeolite pores and on the outer crystal surface. Their crystalline structure and morphology were studied by XRD and scanning electron microscopy. The results showed that in hydrothermal method zeolite acts as a template. CoS nanoparticles with an approximate size of 22 nm grow on the surface of zeolite. In ion exchange method, however, the majority of CoS nanoparticles are about 6 nm in diameter, located on the surface of the MFI (type materials ZSM-5) structure. Exciton absorption peaks at higher energy than the fundamental absorption edge of bulk CoS indicate quantum confinement effect in nanoparticles as a consequence of their small size. The absorption spectra show that the optical band gap for CoS nanoparticles produced by hydrothermal and ion exchange methods is 3.68 and 4.1 eV, respectively.

**Keywords:** CoS nanoparticles, ZSM-5 Zeolite, UV-Vis spectroscopy, Hydrothermal method

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### INTRODUCTION

The design and synthesis of materials with nanometer dimensions in the so-called mesoscopic size range is currently the focus of intense attention because of their considerably different properties from those of the corresponding bulk materials. In particular, samples with particle sizes in the range of 1-10 nm can exhibit novel electronic, optical, magnetic and chemical properties due to their extremely small proportions. These particles have many technological

applications, *e.g.*, in magnetic recording media, Ferro fluids, and catalysts [1-3].

A critical obstacle in assembling and maintaining a nanoscale material is often the high reactivity from the large surface ratio and the spontaneous production of macroscopic-size agglomerates that lack the unique properties of nanoscale particles. In contrast to the conventional preparation methods, the use of an inorganic matrix as a host for nanocrystalline particles can provide an effective way of tailoring a uniform size and controlling the homogeneous dispersion of ultrafine clusters. Cross-linked ion exchange polymer resins, inorganic molecular sieves and sol-gel derived materials have been

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employed as porous hosts for synthesizing nanoparticles [4,5]. These methods offer excellent control of size distribution and morphology through the manipulation of the wet chemical processing parameters, and for the inorganic host structures, higher thermal stability.

Zeolites have attracted much attention because the nanospace within their pores can be used for synthesis of clusters of guest materials. These arrayed clusters have been reported to show new physical properties different from those in the bulk [6,7]. The unique properties of zeolites such as the existence of high intracrystalline surface area with pores of uniform dimensions, the microporous character of the uniformly distributed pores, the ion exchange properties, the ability to develop internal acidity, their thermal stability, and their ability to absorb chemicals/molecules/ionic species into their structure give rise to a great variety of applications which make them significant when compared with other inorganic/polymer materials. Zeolites are a group of materials with nanodimensional pores, which are considered very good templates for preparing quantum dots. 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 zeolite with 10-membered oxygen rings with 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. However, most of microporous materials used as host need a modification procedure to functionalize the micropore internal surface [8,9].

Herein, we would like to report on a systematic investigation of the introduction of cobalt sulfide species into medium-pore MFI-type zeolites. The cobalt sulfide nanoparticles were synthesized by ion exchange of the zeolites in aqueous suspension and by adding cobalt salts to the gels of hydrothermal syntheses in the presence of organic structure agents. It was a particular goal of this investigation to prepare cobalt sulfide nanoparticles located inside and outside zeolite. The analytical tool was used to discriminate between nanoparticles on the surface of the zeolite crystals and inside the zeolite pores. Meanwhile, the zeolite matrix acted as a

templating agent preventing the growth of CoS nanoparticles during the hydrothermal method. CoS nanoparticles by ion exchange methods are located outside zeolite pore.

## EXPERIMENTAL

### Materials and Zeolite Synthesis

All the chemical materials including  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , *etc.*, used in the present work were analytical grade from Fluka or Merck. MFI-type zeolite was synthesized hydrothermally following standard procedures reported in the literature [10]. Zeolite ZSM-5 was synthesized with tetraethyl ammonium hydroxide (TEAOH) as organic agents. The unit cell composition of zeolite, calculated through our obtained EDX data, was  $\text{Na}_{0.3}\text{TEA}_{3.2}[\text{Al}_{3.5}\text{Si}_{92.5}\text{O}_{192}] \cdot 10\text{H}_2\text{O}$ .

### Post-Synthesis CoZSM-5

The ZSM-5 prepared was calcined at 550 °C for 5 h to decompose the template to obtain the white powder. This powder was used as the parent material to prepare CoZSM-5 free template by post synthesis cobaltation method. In this method 0.5 g of ZSM-5 zeolite without template was suspended in 25 ml solution of 0.1 M of cobalt sulfate and stirred at room temperature for 5 h. Then, the samples were washed to remove unexchanged Co ions and dried in air. Prepared sample is called CoZSM-5I. The CoSZM-5I sample was pink in color.

### Hydrothermal Synthesis of CoZSM-5

The CoZSM-5 sample produced by hydrothermal method was obtained from a gel with the molar composition:  $\text{Al}_2\text{O}_3:80\text{SiO}_2:24\text{Na}_2\text{O}:40\text{TEAOH}:30\text{H}_2\text{O}:0.1\text{CoSO}_4$ . The crystallization of the synthesis gel was studied at 175 °C in stainless-steel autoclaves for 62 h under static conditions. The CoSZM-5 sample containing organic templates were calcined in flowing air at 550 °C for 5 h. The CoZSM-5 sample prepared by hydrothermal method was pink in color. This sample is called CoZSM-5A.

### Synthesis of CoSZSM-5

To create the reaction with  $\text{S}^{2-}$  ion, 1 g of both CoZSM-5I and CoZSM-5A samples was added separately to 25 ml of 0.1 M solution of  $\text{Na}_2\text{S}$  at a fixed temperature and magnetically

stirred for 2 h. The samples were washed with deionized water and collected by filtration. The samples are referred to hereafter as CoSZSM-5I and CoSZSM-5A. CoSZSM-5I and CoSZSM-5A samples were fine powders with yellow-green and green color, respectively.

The bulk CoS was also prepared by conventional precipitation method. In this method, an equimolar amount of Na<sub>2</sub>S solution was added dropwise to a stirred solution of 0.1 M CoSO<sub>4</sub> resulting in the formation of bulk precipitates. The obtained CoS precipitates were washed repeatedly with distilled water until freed from S<sup>2-</sup> ions, dried in an air-oven and then calcined at 500 °C for 4h in air. The samples were fine powders with dark color.

### Characterization

The crystallinity of the samples was checked by X-ray diffractometer (Philips X, Pert) with Cu K<sub>α</sub> radiation at room temperature. XRD patterns were recorded using automatic divergence slit system.

Diffuse reflectance spectra were recorded by a scinco 4100 spectrophotometer equipped with an integrating sphere assembly. A special cell loaded with the solid sample was used in all measurements. The spectra were recorded against barium sulfate at room temperature and plotted in terms of absorbance. The UV-Vis spectra were recorded on the same spectrophotometer in their conventional mode.

The specific surface area and pore volume of the samples were measured using a Belsorp-mini II. 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 (SEM) and finally Infrared spectra (IR) on KBr pellet were measured by a Bruker spectrophotometer.

Transmission electron microscopy (TEM) was performed on a Philips EM208 and microscope operated at 100 kV. Samples were prepared by dispersing the powder in ethanol. Imaging was achieved by depositing few drops of suspension on a carbon coated 400 mesh cu grids. The solvent was allowed to evaporate before imaging.

## RESULTS AND DISCUSSION

### X-Ray Diffraction Study

Figure 1 shows the XRD patterns of the samples.

Measurements of the samples were carried out in the 2θ different range, under the conditions of 40 kV and 40 mA, at a step size of 2θ = 0.02°. The XRD patterns show peaks at ranges of 2θ = 7-9° and 23-25°, which correspond to the specific peaks of ZSM-5 zeolite. This indicates that the synthesized ZSM-5 zeolite powders are ZSM-5 zeolite crystals [11].

Nanoparticle samples show similar diffraction peaks indicative of ZSM-5 zeolite. However, some differences, such as the broadening of the diffraction peaks, increase or decrease of some peaks intensity as well as the shift to the peak positions to the lower angle can be observed in the spectra. In fact, the intensities of the (101), (011), (200) and (020) peaks in the CoSAIMCM-41I and CoSAIMCM-41A samples increase and decrease with respect to those of ZSM-5 zeolite, respectively. On the other hand, significant shifts are observed in nanoparticle samples such as peaks at ranges of 2θ = 7-9° shift to 2θ = 6.72-8.75°. In the present patterns there is an increase in some peak intensity when the CoS particles are present in the ZSM-5 zeolite. These peaks are located approximately at 2θ equal to 30°, 36° and 46° which are due to

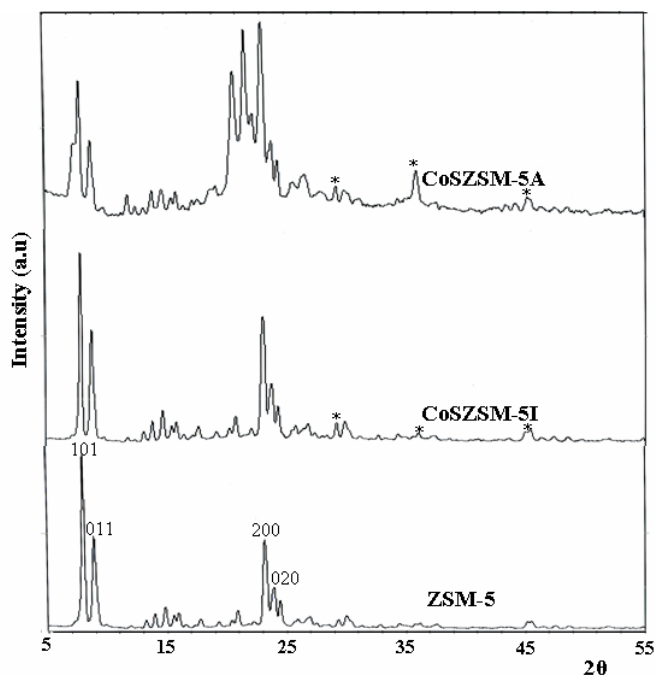


Fig. 1. X-Ray diffraction patterns of the synthesized ZSM-5 and CoS nanoparticles samples.

the reflection of the (100), (101) and (102) planes in the CoS phase, respectively [12]. This difference is in agreement with the reported results for other zeolites [13,14].

### Surface Area and Electron Microscopic Analysis

The specific surface area and pore volume of the CoSZSM-5 samples prepared by different methods are presented in Table 1. As can be seen in Table 1, the surface area of the samples depends on the type of preparation methods. The highest surface area and pore volume were observed for the CoSZSM-5A particles prepared by hydrothermal method. ZSM-5 zeolite is a medium pore size zeolite with a pore opening in the range of 5-6 Å [15]. During the preparation process, CoS particles were homogeneously precipitated inside the pores of the zeolites, and upon removal of the zeolite matrix uniform pores were created in the CoS particles. These pores contribute to a higher pore volume and surface area of the CoSZSM-5A sample. Different results were obtained for CoSZSM-5I sample. The pore volume and surface area of the host zeolite were 0.12 ml g<sup>-1</sup> and 300 m<sup>2</sup> g<sup>-1</sup>, respectively. These values do not change in CoSZSM-5I sample (Table 1). Pores and the specific surface area of the CoSZSM-5I sample demonstrate that the guest (CoS) is located on the surface of ZSM-5 zeolite.

The surface morphology of CoS nanoparticles in zeolite was studied by scanning electron microscopy. The SEM pictures of the CoS samples are presented in Fig. 2. The growth of fine particles of CoS in a regular pattern was observed on the surface of the CoSZSM-5A sample in Fig. 2. The surface was also relatively smooth for the CoS particles prepared from the zeolite matrix by hydrothermal method. The SEM study clearly demonstrates nanosize CoS as a template for synthesis by hydrothermal method. The SEM picture of

unloaded ZSM-5 zeolite and the prepared composite material by ion exchange method show that lath shape of the ZSM-5 zeolite crystallites is not affected by the CoS loading. These micrographs for CoSZSM-5I sample also show CoS nanoparticles outside the zeolite.

The TEM images of CoSZSM-5I and CoSZSM-5A samples as shown in Fig. 3. In CoSZSM-5I sample (Fig. 3a) the nanoparticles have a well-defined spherical shape and tend to accumulate to form larger CoS aggregates. Both features of CoS nanoparticles in ZSM-5 zeolite, i.e. the spherical shape and the tendency to aggregate, were also observed in TEM micrographs of CoS nanoparticles in solution [16]. With respect to individual nanoparticles it was estimated that their average size was about 5 nm. Fig. 3b shows TEM image of CoSZSM-5A sample. The products of CoS nanoparticles are all found to be spherical and their average nanoparticle size is about 24 nm. However, CoS nanoparticles in CoSZSM-5A sample exhibit that they can easily aggregate (similar to CoSZSM-5I sample) due to their small dimensions and high surface area.

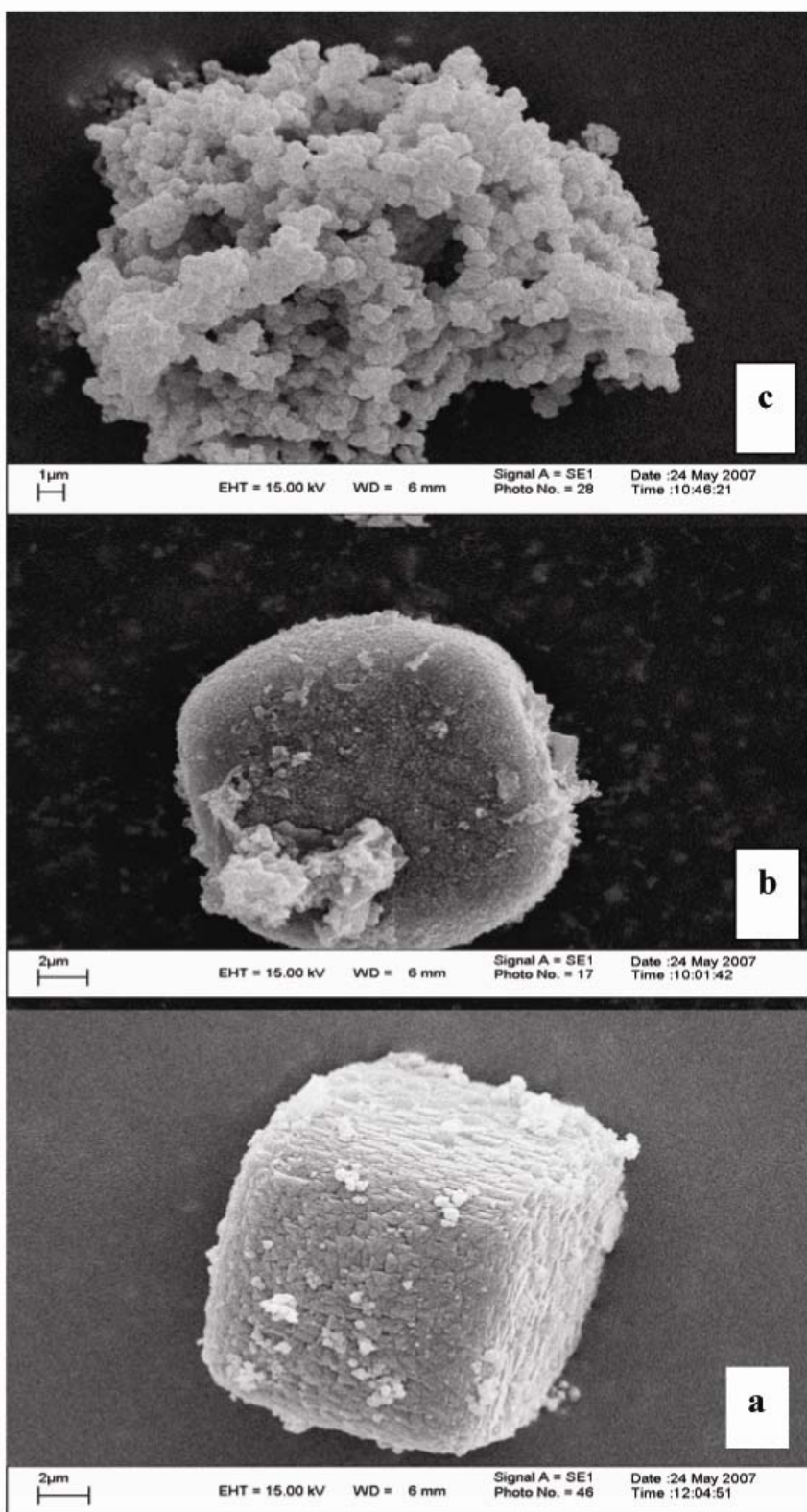
### UV-Vis Spectra

Diffuse reflectance spectra for CoS nanoparticles in ZSM-5 zeolite, prepared by different methods, are shown in Fig. 4. Comparing the absorption edge of bulk CoS with that of CoSZSM-5I and CoSZSM-5A samples shows that a blue shift in the onset of absorption is observed in these samples. This phenomenon of blue shift of absorption edge has been ascribed to a decrease in particle size. It is well known in case of semiconductors that the band gap between the valence and conduction band increases as the size of the particles decreases in the nanosize range. The magnitude of the shift depends on the size of the semiconductor. In the present study, the

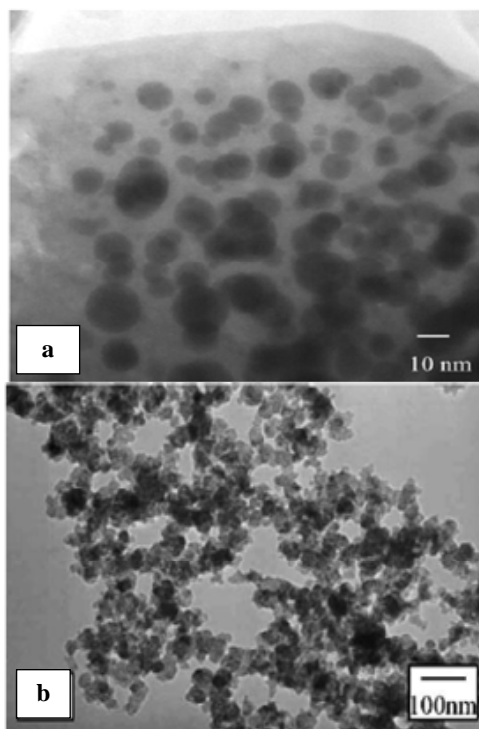
**Table 1.** Band Gap, Specific Surface Area (BET), Pore Volume and Absorption Edge of CoSZSM-5I and CoSZSM-5A Samples Prepared from Zeolite and Bulk CoS Sample

Sample	Band gap (eV)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Particle size (nm)	Pore volume (ml g <sup>-1</sup> )	Absorption edge (nm)
ZSM-5	-	300	-	0.12	-
CoSZSM-5I	4.10	298	6	0.11	305
CoSZSM-5A	3.68	340	22	0.14	340
CoS bulk	3.91	14	18	0.04	320

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**Fig. 2.** Scanning electron micrographs of ZSM-5 (a), CoSZSM-5I (b) and CoSZSM-5A (c).

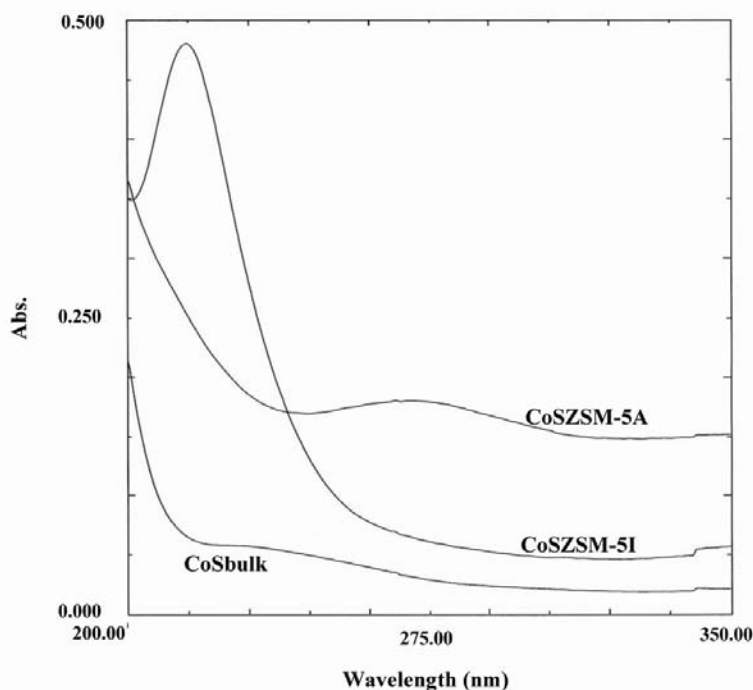


**Fig. 3.** Transmission electron microscopy (TEM) images of CoSZSM-5I (a) and CoSZSM-5A (b) samples.

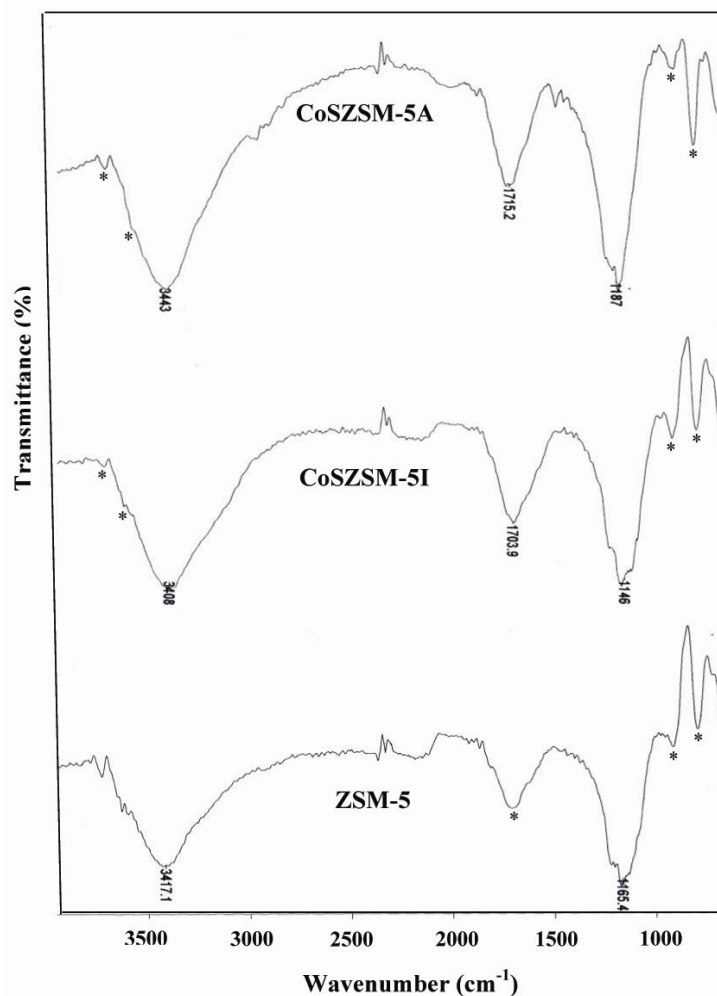
CoSZSM-5I and CoSZSM-5A samples show a blue and red shift approximately 15 and 20 nm compared to the bulk particles respectively. Calculated by the Kayanuma model [17] the estimated size of these CoS nanoparticles were 22, 18 and 6 nm for CoSZSM-5A, CoS bulk and CoSZSM-5I samples, respectively. The estimated size of CoS nanoparticles also calculated by Kayanuma model was similar to TEM results. From the onset of the absorption edge, the band gap of the CoS particles was calculated using the method of Tandon and Gupta [18]. In Table 1, the band gap is found to increase in the order of CoSZSM-5I > CoS bulk > CoSZSM-5A.

### IR Spectra

The IR spectra of ZSM-5, CoSZSM-5I and CoSZSM-5A samples in the range of 800-4000  $\text{cm}^{-1}$  are shown in Fig. 5. The IR spectrum of ZSM-5 shows bands at 814, 905, 1165.4 and 1722  $\text{cm}^{-1}$  which are assigned to different vibrations of tetrahedral and framework atoms in ZSM-5 zeolite [19,20]. The spectrum of OH-groups in the parent ZSM-5 shows bands at 3730, 3690 and 3417  $\text{cm}^{-1}$  which belong to isolated Si-OH, nano-framework Al, and acidic bridged hydroxyls, respectively [21].



**Fig. 4.** Diffuse reflectance spectra for the set of CoS samples.



**Fig. 5.** IR spectra of ZSM-5 and CoS nanoparticles zeolite.

In the present work, all bands in CoSZSM-5I and CoSZSM-5A samples show a shift to lower and higher wave numbers with respect to the ZSM-5 zeolite, respectively. This shift reveals that nanoparticles could incorporate into ZSM-5 zeolite. Increased intensity is observed in both nanoparticle samples with respect to ZSM-5 zeolite. This increase is related to extension of perturbation of T-O-T vibrations of the zeolite lattice (bands 1700-800  $\text{cm}^{-1}$ ) and acidic bridged hydroxyls vibrations (3417  $\text{cm}^{-1}$  band) [22]. Meanwhile, the existence of the bands at 3730 and 3690  $\text{cm}^{-1}$  in ZSM-5 implies decrease in intensity of the nanoparticles sample due to  $\text{SiO}_2/\text{Al}$  ratio (aluminum loss) in order to replace non-framework Al by the corresponding metal ion increase. The reaction of ZSM-5

zeolite with cobalt sulfate solution replaces non-framework Al by Co cation. As a result, significant decrease was observed in the intensity of these bands (free Si-OH and non-framework Al). These kinds of differences are related to the presence of CoS nanoparticles in zeolite.

## CONCLUSIONS

The CoSZSM-5 samples were prepared by hydrothermal and ion exchange methods. The prepared nanoparticles were characterized by powder XRD, chemical analysis, adsorption technique and infrared spectroscopy. The results show that in hydrothermal method, zeolite matrix acts as a templating agent

whereas CoS nanoparticles grow on the surface area of ZSM-5 zeolite in ion exchange method. Particles size was 22 and 6 nm for CoS nanoparticles in ZSM-5 zeolite matrix obtained by hydrothermal and ion exchange methods, respectively.

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