

Ni and Co Substituted Zinc Ferri-chromite: A Study of their Influence in Photocatalytic Performance

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Abstract

Enhanced photocatalytic activity was demonstrated in the present study for two systems i.e., $Zn_{1-x}Ni_xFeCrO_4$ and $Zn_{1-x}Co_xFeCrO_4$ ($0.0 \leq x \leq 1.0$) in photo degradation of methyl orange, methyl red and congo red dyes. The basic aim of this study is to find a suitable compound of doped zinc ferrichromite as photocatalyst for degradation of organic dyes. A sol-gel process used for synthesis of crystalline nanopowders gave better photocatalytic activity under the UV light radiations. The result showed that, dyes undergo fast degradation with UV light in presence of doped compounds. The rate of degradation of dyes was estimated spectro-photometrically from residual concentration in dyes.

Keywords: Sol-gel synthesis; Surface area; Pore volume; Photocatalytic activity

Introduction

In the compounds of mixed metal oxides, spinel ferrites find wide applications in both technological and catalytic field. Spinel of AB_2O_4 type, where 'A' and 'B' are tetrahedral and octahedral symmetric oxygen sites containing divalent or trivalent cations have been studied for their innumerable technological applications such as transformer cores, micro-devices in radio frequency coils due to excellent magnetic properties, low magnetic coercivity, high resistivity, small eddy current losses, high curie temperature and chemical stability [1-4]. Their properties like crystal structure, electronic conduction, magnetism and catalytic activities are depends upon the type of magnetic ions residing in A- or B-sites and their sublattice interactions. In the potential applications of Ni and Co based soft ferrites, especially where these elements are partially substituted for zinc in spinel lattice strongly affect the properties of Ferro spinel. $ZnFeCrO_4$ a normal spinel and its degree of inversion depends upon nature of substituted cations. However if A-site get occupied by diamagnetic ion, then B-B interaction become quit predominant. Ni-Zn ferrite or Co-Zn ferrite are inverse spinel where Zn^{2+} ions are present in tetrahedral site while octahedral site is occupied by Ni^{2+} , Co^{2+} , Fe^{2+} and Fe^{3+} ions. The catalytic activity is because of the migration of metallic ions between sub lattices which do not alter a basic structure and makes a catalyst more effective for reactions [5,6].

During recent years, photo catalytic oxidation of dyes using ferrites has gained enormous interest. Most of the dyes used in the pigmentation of leather, textiles, paper, ceramics, cosmetics, inks and food-processing products are derived from azo dyes, which are characterized by the presence of one or more azo groups ($-N=N-$) in their structure. But during synthesis and processing of materials, much of the dyes get waste within water. Because of toxic nature of azo dyes, this waste produces a great hazard to human and environmental health. Therefore, it is a challenge to researchers for effective removal of dyes of wastewater from industries. Hence for degradation of polluted waste water containing both toxic and non-biodegradable compounds, the development of suitable process is needed [7,8]. The study on ferrosinels based Ni and Co substituted zinc ferrichromites for their structural characterization and electronic properties was recently reported [9,10]. This work is again extended to utilize the synthesized compounds as photocatalysts for degradation of some organic dyes and to determine the detailed degradation kinetics.

Experimental Details

Nanocrystalline Ni and Co doped ferrichromites were prepared separately by sol-gel auto-combustion method using A.R. grade

nitrate salts of Fe, Zn, Cr, Ni and Co. For the preparation of system $Zn_{1-x}Ni_xFeCrO_4$ ($0.0 \leq x \leq 1.0$), calculated amount of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) were weighed according to required stoichiometry and dissolved separately in deionized water to obtain a clear solution. An equimolar solution of citric acid was then added to all solution and heated at $80^\circ C$ to about 30 minute under constant stirring. After the solutions to clear and transparent, a small quantity of ammonia was added into the solutions to adjust pH-7-8. Then all solutions were poured into a tray and heated slowly to $110^\circ C$ which turned into porous dry gel. This mixture was continuously evaporated to almost dryness to obtain a homogeneous uniform material. Here precursors undergo a strong auto-combustion process during ignition of dried gel [11]. The same method was followed for preparation of system $Zn_{1-x}Co_xFeCrO_4$ ($0.0 \leq x \leq 1.0$) where cobalt nitrate ($Co(NO_3)_2 \cdot 9H_2O$) was used instead of nickel nitrate. All the dried citrate compounds were calcinated separately at $800^\circ C$ for 6 h (first monitored from TGA-DTA) to breakdown the citrate gel complexes into spinel oxides. Surface area by Brunauer-Emmett-Teller (BET) technique and pore volume distribution for the samples of good activity were obtained by employing nitrogen as adsorbing gas. Initially, samples were regenerated for degassing at $150^\circ C$ for 1 h and the data were measured using Smart instrument: Model Smart-Sorb 92/93 surface area and pore volume analyzer with the help of liquid nitrogen (77K) and water (300K) atmospheres for both adsorption and desorption of N_2 . The photocatalytic activities of synthesized compounds were tested by using anionic dyes such as 10 ppm methyl orange (MO), 10 ppm methyl red (MR) and 5 ppm congo red (CR) solutions for their decolorisation and degradation process. These dye solutions were used as a test contaminant since it has been extensively used as an indicator for the photocatalytic activities owing to its absorption peaks in the visible range. Hence its degradation can be easily monitored by optical absorption spectroscopy. A 100 ml volume of dye in aqueous solution with 100 mg of catalyst was used in all

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experiments. The photoreactor consist of a jacketed quartz tube in which a high pressure mercury vapor lamp of 125 W power was placed. At the first, photolysis was also carried for dyes solution using UV radiations without photocatalyst. Prior to irradiation, the suspensions were continuously stirred in the dark for 60 min to ensure the establishment of an adsorption/desorption equilibrium. Then the reactor was irradiated with UV light corresponding to their absorption wavelength. The distance between a lamp and center of the beaker was kept at 8-10 cm. About 2-3 ml of sample was taken at 15 minute intervals of time up to 90 minute. Before measurement, all the samples were centrifuged for 5 minute. The course of degradation reaction and concentration of dye in samples were monitored at regular intervals of time using a UV-Visible spectrophotometer.

Results and Discussion

Photocatalytic activity

The photocatalytic activity of synthesized samples under UV light was evaluated by performing experiments on the degradation of MO, MR and CR in aqueous solution. Figure 1 illustrates the degradation of these dyes by photocatalysis in the presence of different Ni and Co substituted zinc ferri-chromites for one hour. The results showed that, the concentration of dye solution barely changed after a solution had been directly illuminated. The absorption peaks of dyes became weaker along with the irradiation time and hence azo groups as well as aromatic part of the dyes molecule were destructed under UV light. This indicates the zinc substitution by nickel and cobalt in ferri-chromite increase the photocatalytic degradation of dyes. It was found that MO degraded to 30% by catalyst $Zn_{0.4}Ni_{0.6}FeCrO_4$, MR degraded to 20% by same catalyst while CR degraded to 45% by catalyst $Zn_{0.2}Ni_{0.8}FeCrO_4$ after one hour. For Co doped zinc ferri-chromites, MO degraded to 70% by catalyst $Zn_{0.4}Co_{0.6}FeCrO_4$, MR degraded to 40% by same catalyst while CR degraded to 15% by catalyst $Zn_{0.6}Co_{0.4}FeCrO_4$ after one and half hour. This could be explained on the basis of smaller crystallite size and optimal concentration of substituted ions in zinc ferri-chromite for more efficient separation of photo-induced electron-hole pairs. If substitution increases, the surface barrier becomes higher and a space charge region becomes narrower [12-14]. Both Ni^{2+} and Co^{2+} have more partially filled d-orbitals and provide an effective recombination center for electrons and holes. There is more catalysts surface area for absorption of photon and interaction of molecules of reactants with catalyst, due to which number of holes, hydroxyl radicals and supra oxide ions get increased. But with increase in content of doped ions over optimal point i.e., when the substitution content exceeds ($x \geq 0.8$), the space charge region becomes nar-rower and photo-generated electron-hole pair recombination take place, leading to decreased photocatalytic activity of system. In addition, it affects the optical and electronic properties and presumably shift the optical absorption towards the visible region [15-18]. Other reasons of activity of compounds are the surface area, crystallite size, phase purity and surface defects on surface layer. The measured BET surface areas and pore volumes of the active photocatalysts are given in Table 1. Due to different degrees of agglomeration of grains and number of fine pores, an average surface area is found to be $70 \text{ m}^2\text{g}^{-1}$. The substituted Ni and Co ions have partially filled d-orbitals. Hence their doping in

$ZnFeCrO_4$ produces the surface defects. At higher concentration of substitution, there is a remarkable change in surface area and pore size as the substituted ions occupies the pores. This may be attributed to sintering process and increasing crystallite size. By measuring an absorbance with irradiation time, the concentrations of degraded dyes were determined for which the catalysts show high degree of decolorisation and degradation. Figure 2 shows the plots of $\ln C/C_0$ against irradiation time from which kinetic rate constant (k) of degradation of dyes was calculated by

$$\ln C/C_0 = -k \times t$$

C_0 : dye concentration at $t=0$

C : concentration at time t .

These time varying degradation rates for used photocatalyst are shown in Table 1.

Reusability of photocatalyst

The spent catalysts were tested for its reusability and stability after separating the catalysts from the reactant solution by centrifugation, washing and drying at 120°C in an oven. Their structure was further examined by XRD and SEM image. It was found that there is no much more change in the structure and morphology of used catalyst. The peaks of XRD patterns were again well indexed by Bragg's law showing fundamental peaks of single phase face centered cubic spinel structure. The used catalysts were found to a well-defined crystalline phase as they have before the catalysis. The morphological images visualized by SEM also exhibit an intergranular porosity and the absence of internal pores. The intergranular pores are linked through large pores and this porous structure favors the adsorption and condensation of dye solutions [9,10]. Figures 3 and 4 shows the X-ray pattern and SEM images of used catalysts in photodegradation of dyes.

Conclusions

The progress of photocatalytic study of dyes shows that the facile sol-gel synthesized Ni and Co substituted zinc ferrichromites are the effective catalysts in decolorisation and degradation of methyl orange, methyl red and congo red under UV irradiation. The activity of substituted Ni and Co ferrichromites is due to increased optical absorption and increase life time of charge carriers. These recyclable photocatalyst are reusable as there is no more major change in their structure after photocatalysis.

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Compound	Surface area $\text{m}^2 \cdot \text{g}^{-1}$	Pore volume $\text{cc} \cdot \text{g}^{-1}$	Kinetic rate constant (k) min^{-1}
$Zn_{0.4}Ni_{0.6}FeCrO_4$	68	0.11	0.0049 for MO and 0.004 for MR
$Zn_{0.2}Ni_{0.8}FeCrO_4$	76	0.15	0.00861 for CR
$Zn_{0.4}Co_{0.6}FeCrO_4$	72	0.13	0.00298 for MO and 0.011 for MR
$Zn_{0.6}Co_{0.4}FeCrO_4$	66	0.09	0.015 for CR

Table 1: Surface area, pore volume and kinetic rate constant for degradation of dyes of compounds which works as effective photocatalyst.

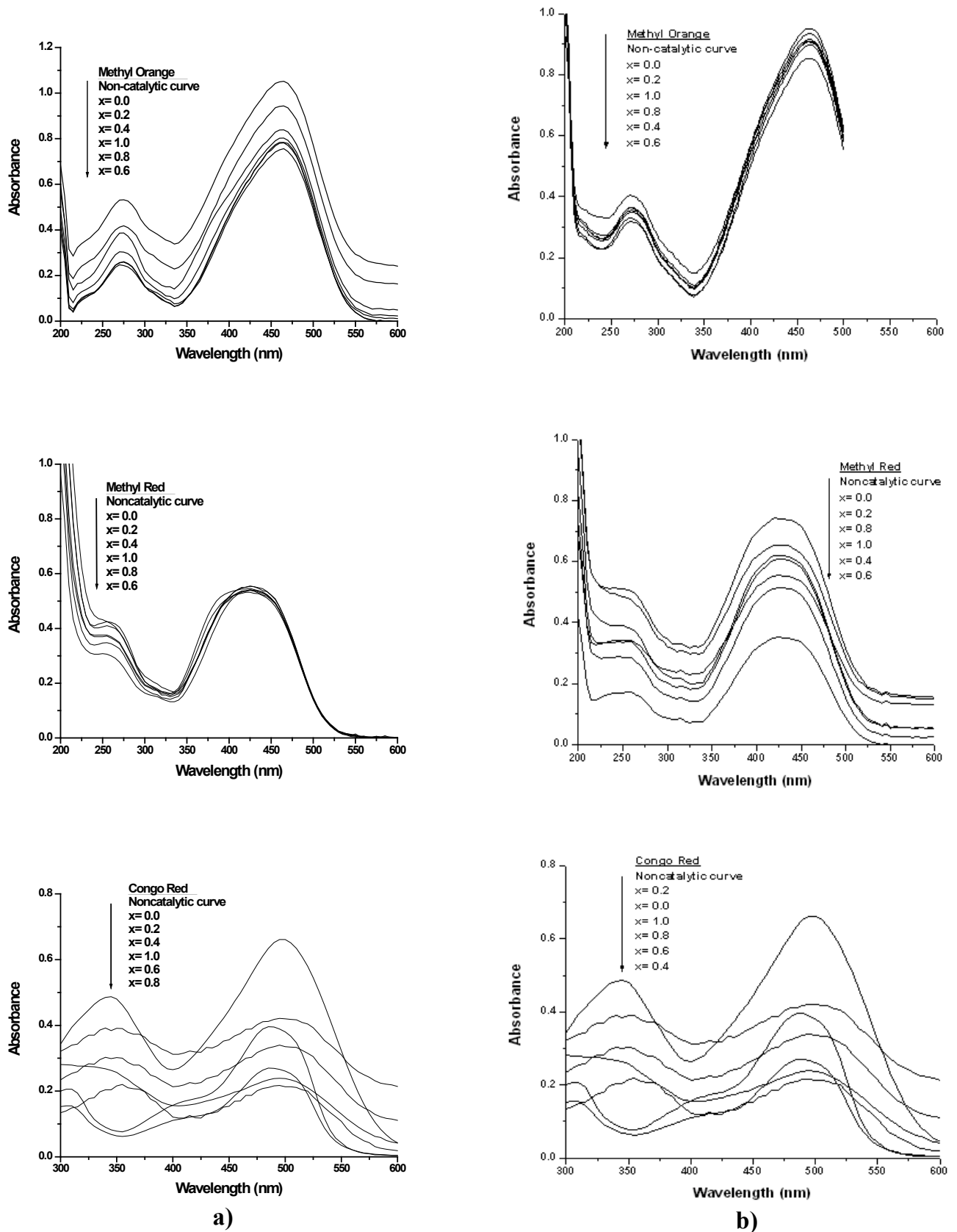


Figure 1: Photodegradation of the MO, MR and CR dyes using a) Ni b) Co doped photocatalyst ($0.0 \leq x \leq 1.0$) after one hour UV irradiation.

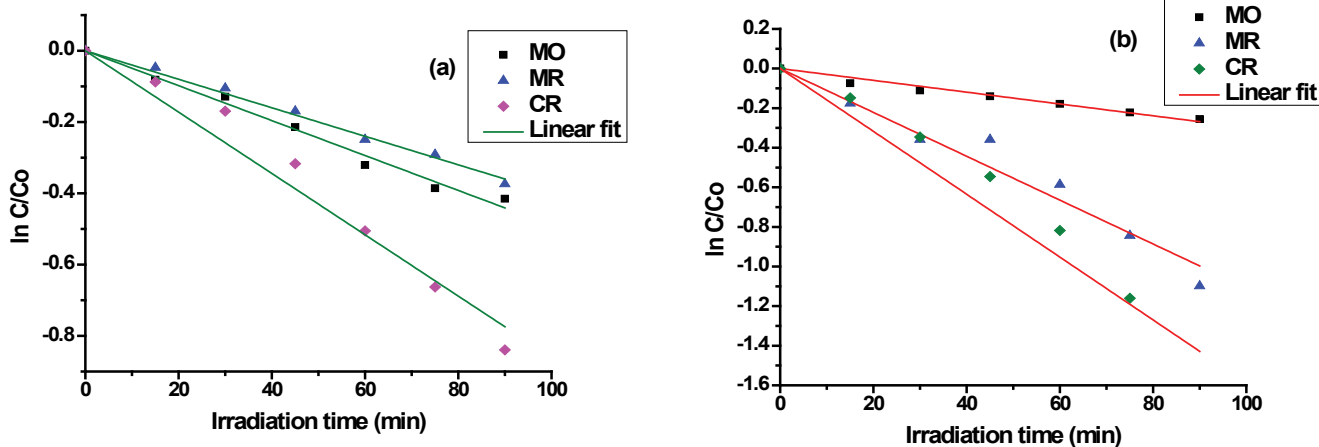


Figure 2: Graph of $\ln C/Co$ Vs irradiation time for a) Ni b) Co doped used photocatalyst.

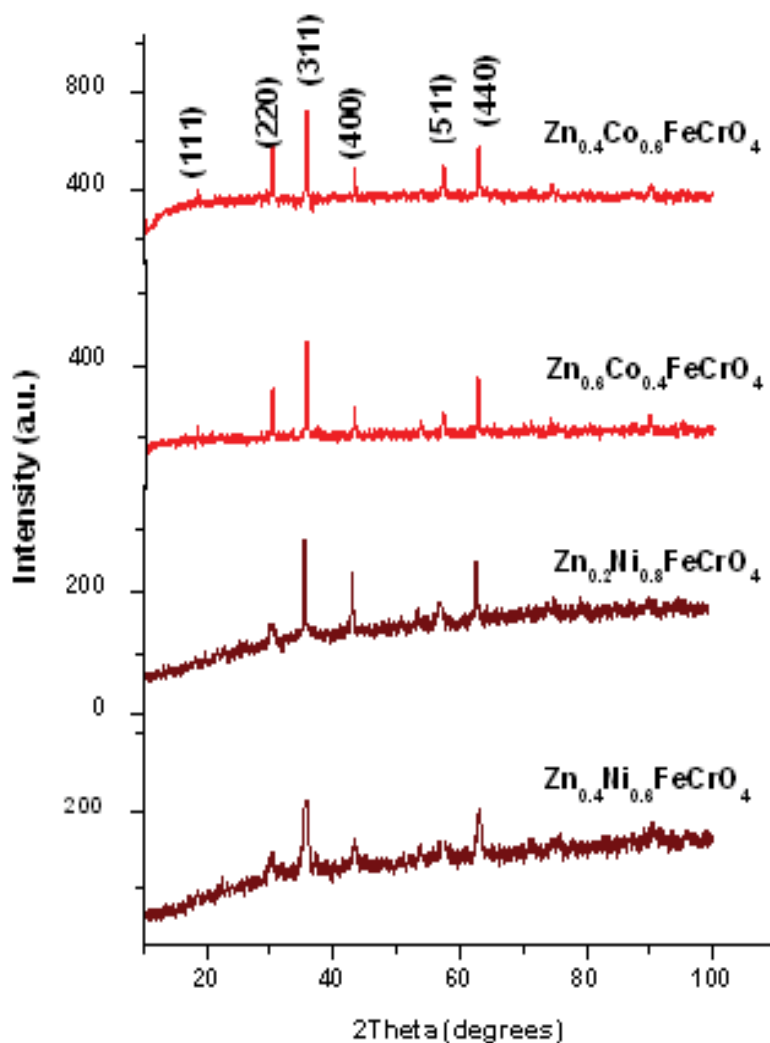
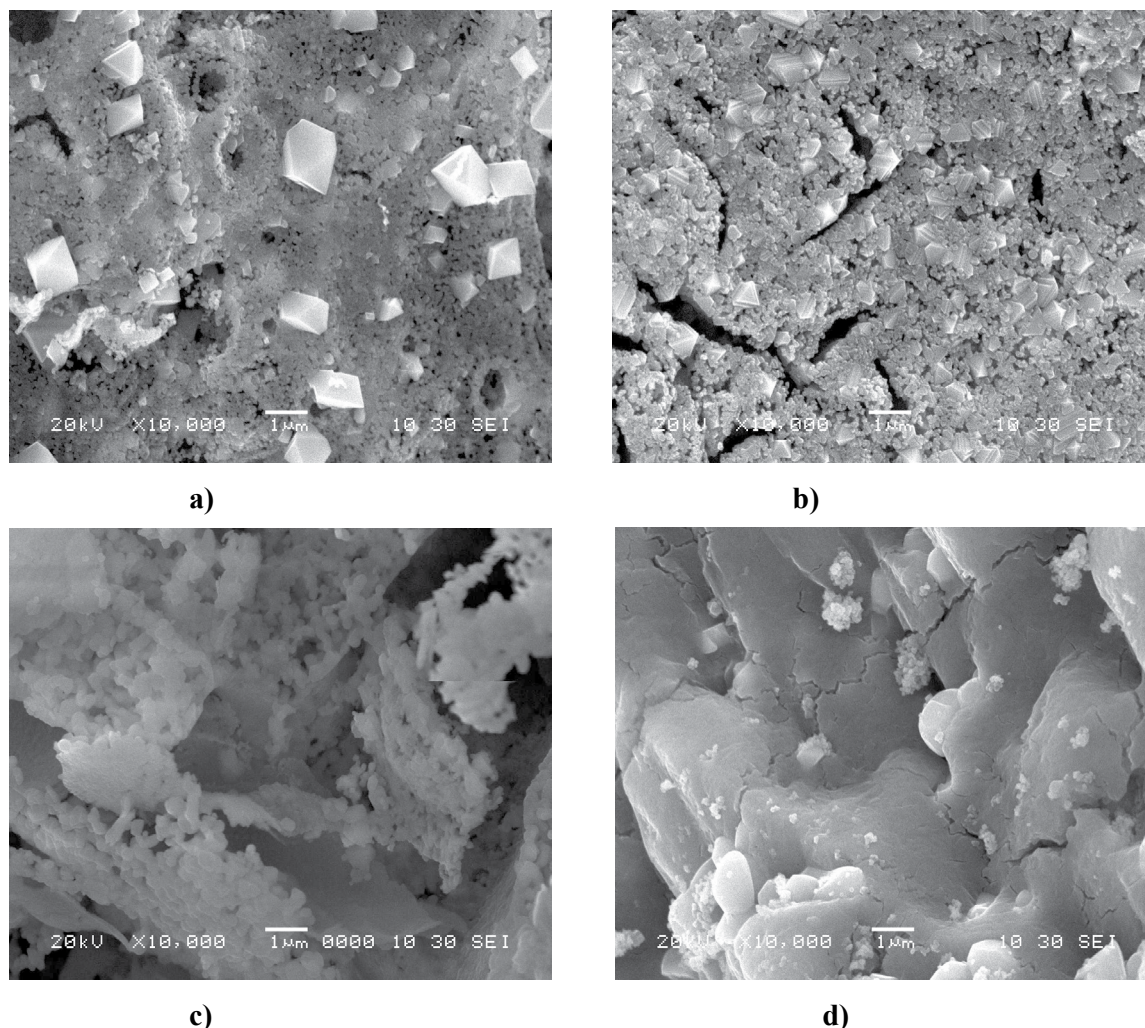


Figure 3: X-ray diffraction patterns of compounds after photocatalysis.



a) $Zn_{0.4}Ni_{0.6}FeCrO_4$ b) $Zn_{0.2}Ni_{0.8}FeCrO_4$
c) $Zn_{0.6}Co_{0.4}FeCrO_4$ d) $Zn_{0.4}Co_{0.6}FeCrO_4$

Figure 4: Surface morphology by SEM of used compounds after photocatalysis.

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