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Preparation and Investigation of Spinel-structured $FeCo_2O_4$ Nanoparticles as an Efficient Catalyst for Oxidation of Sulfides

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We report the preparation and characterization of spinel-structured $FeCo_2O_4$ nanoparticles for the efficient and selective oxidation of sulfides. The as-prepared $FeCo_2O_4$ nanoparticles were characterized by powder X-ray diffraction (PXRD), energy-dispersive X-ray analysis (EDX), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). According to TEM images, the size of the $FeCo_2O_4$ particles is identified to be 10-20 nm. The obtained $FeCo_2O_4$ nanoparticles were used as an efficient catalyst for oxidation of sulfides. For all sulfide substrates, very good conversions (69-100%) and selectivities (89-99%) depending on the nature of the sulfide substrates were obtained. The reusability and recoverability of catalyst show that the catalytic system can be reused fourth times without significant loss of reactivity and stability.

Keywords: Nanoparticles, Spinel, $FeCo_2O_4$, Oxidation, Sulfide

INTRODUCTION

Catalytic oxidation of sulfides for producing sulfoxides as very important and significant intermediates has been known as one of the most important chemical transformations in chemistry [1-7]. Among all the materials to be used as a catalyst for synthesis, oxidation reactions catalyzed by transition metal oxide have been attracted widespread attention in organic synthesis [8-15].

Mixed binary transition metal oxides MCo_2O_4 (M = Fe, Ni, Cu, Mn and Zn) attracted much consideration in solid state sciences due to their outstanding performance as catalysts, magnetic and anode materials, semiconductors and pigments [16-20]. Iron cobaltite, $FeCo_2O_4$, is the promising transition metal oxide in the family of cobaltite materials which have attracted considerable attention in the synthesis due to easy availability, economical cost and environmental benignity [21-23].

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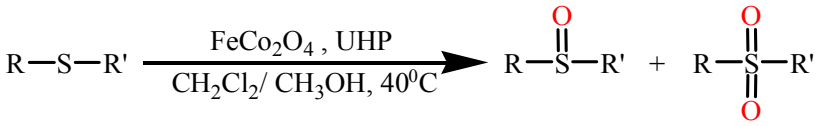
In this paper, we report the preparation of binary spinel iron cobaltite, $FeCo_2O_4$, and examine their catalytic activity on the selective oxidation of sulfides to corresponding sulfoxides in the presence of urea hydrogen peroxide (UHP) as an oxidant under moderate reaction condition (Scheme 1).

EXPERIMENTAL

Chemicals and solvents were purchased from the Fluka and Merck Chemical companies without further purification. ZIF-67 powder was synthesized according to a published method [24].

Synthesis of the $FeCo_2O_4$ Nanoparticles

In a conventional procedure, in 20 ml of ethanol including 80 mg of $Fe(NO_3)_2{\cdot}6H_2O$, 40 mg of ZIF-67 powder was first dispersed and stirred for 30 min to form a homogeneous suspension of Fe-Co precursor. The as-obtained powders were collected by centrifugation and dried



Scheme 1. The oxidation of sulfides by the $FeCo_2O_4$/UHP catalytic system

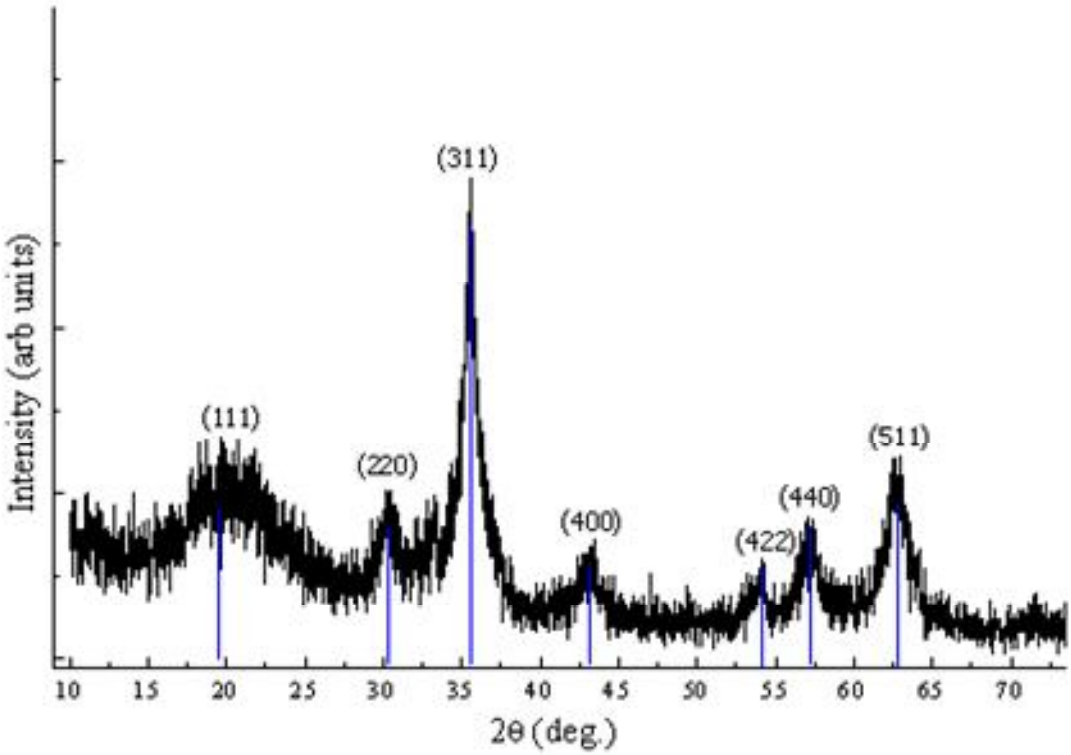


Fig. 1. Typical XRD pattern of the as-prepared $FeCo_2O_4$ nanoparticles.

at 70 °C for 10 h. Then the $FeCo_2O_4$ nanoparticles were collected as black powders by tempering the as-obtained Fe-Co precursor in the air at 350 °C for 2 h.

Catalytic Sulfoxidation

To a stirred mixture of $FeCo_2O_4$ nanoparticles and sulfide (0.2 mmol) and chlorobenzene (0.2 mmol) as an internal standard in 1 ml of (1:1) mixture of CH_3OH/CH_2Cl_2 was added gently 0.4 mmol UHP as an oxidant. Stirring was maintained for 4 h and the reaction progress was monitored by GC. Assignments of the products were gained by comparison with authentic samples.

RESULTS AND DISCUSSION

Structural and Morphological Characterizations

The XRD patterns of the as-prepared $FeCo_2O_4$ nanoparticles are demonstrated in Fig. 1. The peaks at 2θ = 19.1°, 30.3°, 35.6°, 43.2°, 54.1°, 57.3° and 62.7° can be attributed to (111), (220), (311), (400), (422), (440) and (511) reflections of the cubic structure of the $FeCo_2O_4$ spinel phase with Fd3m spacegroup and JCPDS card no. 98-001-6669 [25]. These diffraction patterns clearly verify the phase purity of as-prepared $FeCo_2O_4$ nanoparticles and show good agreement with earlier reports [26,27]. Energy

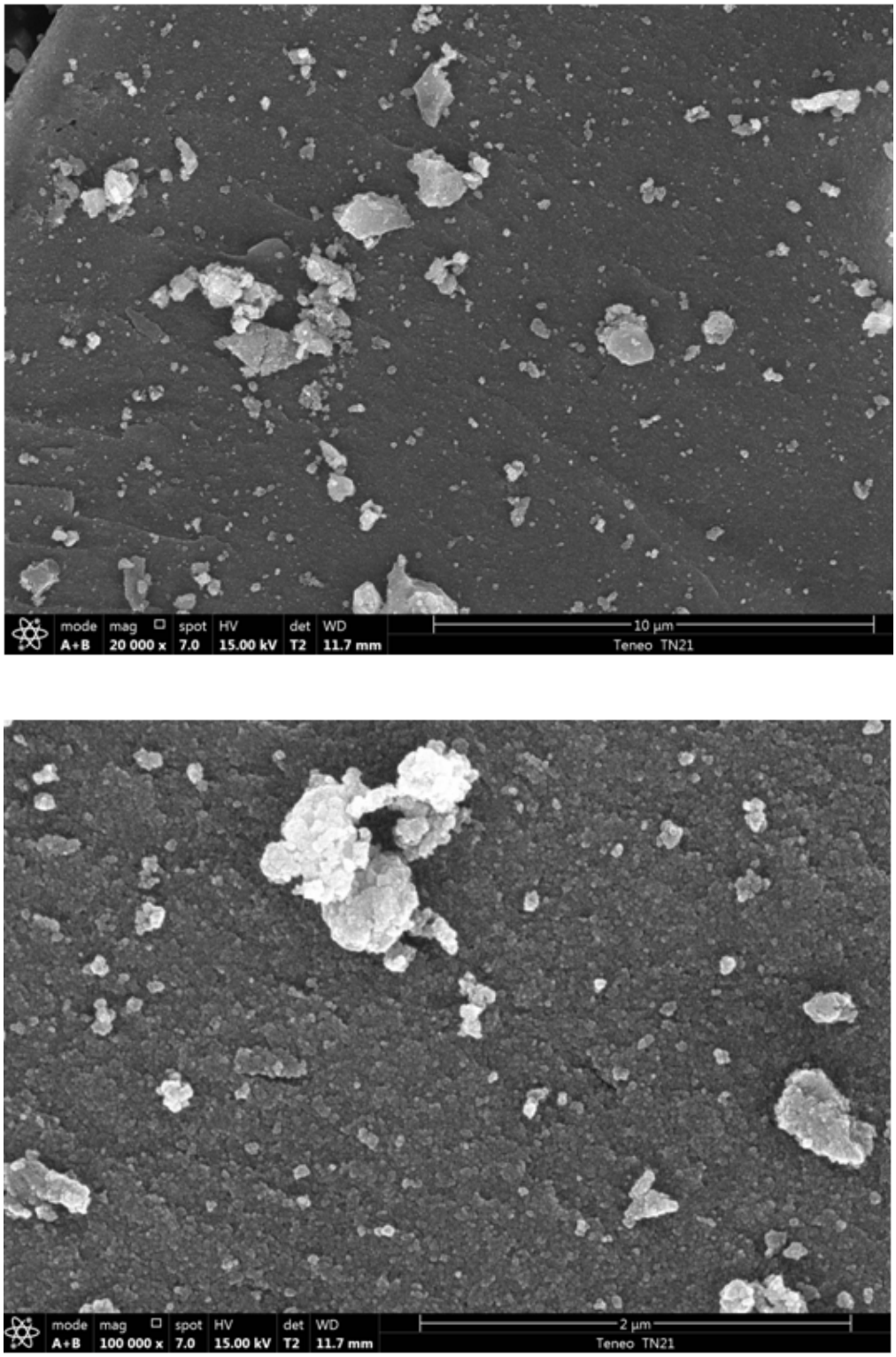


Fig. 2. SEM images of the the as-prepared $FeCo_2O_4$ nanoparticles.

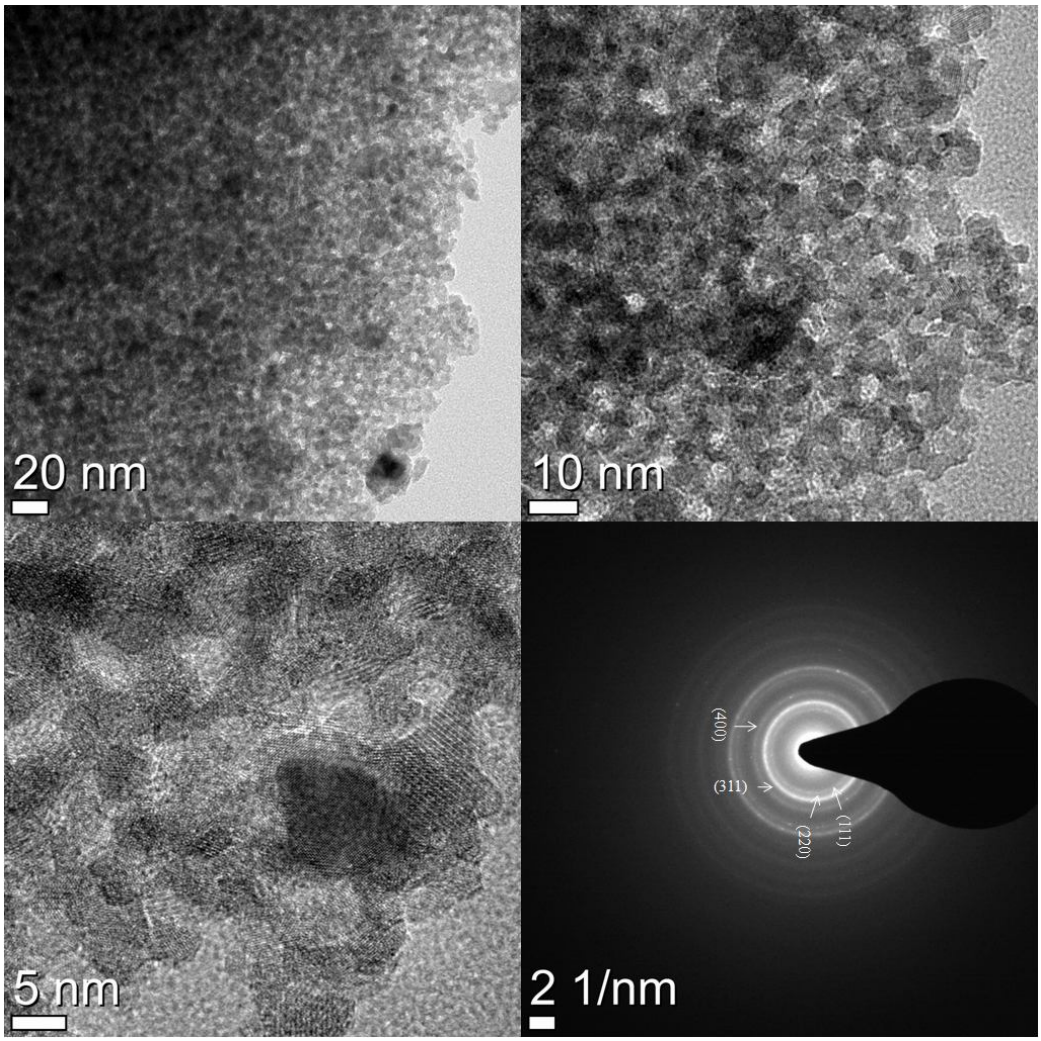


Fig. 3. TEM images of the as-prepared $FeCo_2O_4$ nanoparticles.

Dispersive X-Ray (EDX) analysis of the as-prepared $FeCo_2O_4$ nanoparticles pointed that the composites consisted of cobalt, iron, and oxygen.

Figure 2 depicts the surface morphology of the $FeCo_2O_4$ nanoparticles. The SEM images show the formation of $FeCo_2O_4$ particles with diameters in the range of nanometers.

For further understanding of the $FeCo_2O_4$ nanoparticles microstructure and morphology, transmission electron microscopy (TEM) analysis was also carried out. As seen in Fig. 3, the size of the $FeCo_2O_4$ particles could be identified to be 10-20 nm.

Catalytic Activity

In order to optimize the reaction conditions in the sulfide oxidation, we initially carried out the oxidation of methylphenylsulfide (MPS) in the presence of as-prepared $FeCo_2O_4$ nanoparticles using UHP as an oxidant. First, the reaction was conducted without any catalyst and an only trace amount of sulfoxide was obtained. Catalyst loading tests were performed in order to find out the lowest amount of catalyst for efficient oxidation of sulfides. Therefore different catalyst amounts were tested in (1:1) mixture of CH_3OH/CH_2Cl_2 and UHP and the results are summarized in Fig. 4. With increasing the amount of nanoparticles from

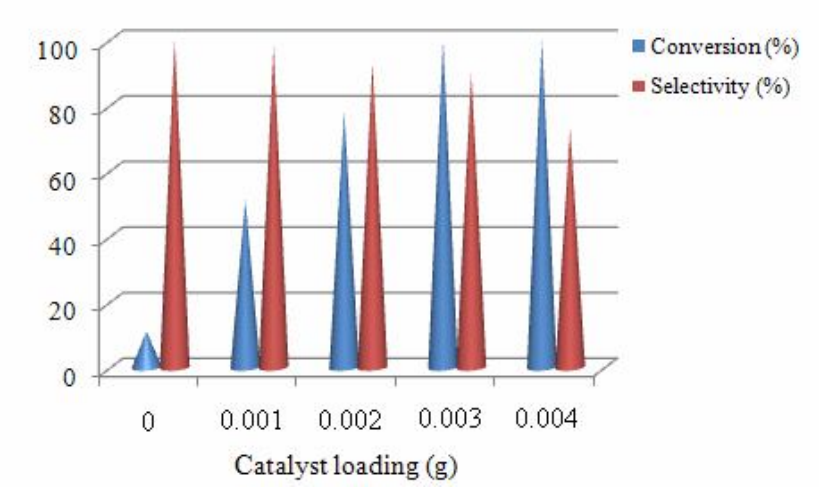


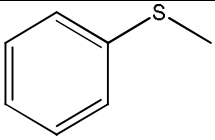
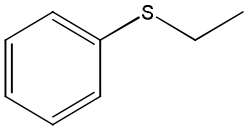
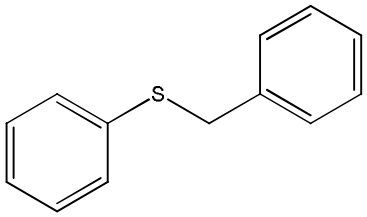
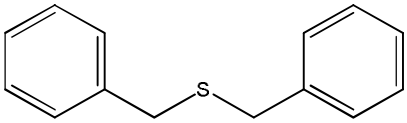
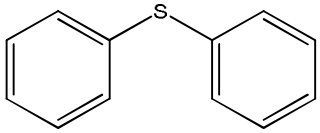
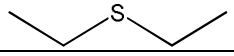
Fig. 4. Catalyst amount effect on the oxidation of MPS .Reaction conditions: MPS/UHP (mol mol^{-1}) = 1/1; solvent: MeOH/CH_2Cl_2; reaction temperature: 40 °C; reaction time: 4 h.

Table 1. Oxidation of Methylphenylsulfide in Different Conditions[a]

Entry	Solvent	Reaction temperature (°C)	Reaction time (h)	Conversion (%)[b]	Selectivity (%)[c]
1	CH_2Cl_2	40	4	43	99
2	CH_3OH	40	4	61	97
3	CH_3OH/CH_2Cl_2	40	4	100	90
4	CH_3CN	40	4	55	97
5	C_6H_{12}	40	4	7	100
6	H_2O	40	4	41	85
7	CH_3OH/CH_2Cl_2	r.t.	4	48	99
8	CH_3OH/CH_2Cl_2	30	4	85	92
9	CH_3OH/CH_2Cl_2	Reflux	4	100	85
10	CH_3OH/CH_2Cl_2	40	2	54	97
11	CH_3OH/CH_2Cl_2	40	3	84	93
12	CH_3OH/CH_2Cl_2	40	5	100	61

[a]Reaction conditions: 1 ml of solvent; 0.2 mmol of methylphenylsulfide; 0.2 mmol UHP; 0.003 g $FeCo_2O_4$ nanoparticles. [b]Determined by GC on the crude reaction mixture. [c]Selectivity to sulfoxide = (sulfoxide%/(sulfoxide% + sulfone%)) × 100.

Table 2. Oxidation of Sulfides with UHP Catalyzed by $FeCo_2O_4$ Nanoparticles[a]

Entry	Substrate	Conversion (%)[b]	TON[c]	Selectivity (%)[d]
1		100	15.7	90
2		99	15.6	91
3		97	15.4	89
4		89	14.01	96
5		75	11.8	95
6		69	10.9	99

[a]Reaction conditions: 1 ml of CH_2Cl_2/CH_3OH; 0.2 mmol of substrate; 0.2 mmol UHP; 0.003 g $FeCo_2O_4$ nanoparticles. [b]Determined by GC on the crude reaction mixture. [c]TON = mol product/ mol catalyst. [d]Selectivity to sulfoxide = (sulfoxide%/ (sulfoxide% + sulfone%)) × 100.

0.001 g to 0.003 g, the conversion of MPS increased from 51 to 100%. But with a high loading of catalyst, the selectivity of MPS decreases from 90% to 73%. Thus optimized amount (0.003 g) of $FeCo_2O_4$ nanoparticles was used for all of the oxidation reaction.

The solvent effect on the oxidation reaction of MPS has been studied using various solvents *viz* CH_2Cl_2, CH_3OH, CH_2Cl_2/CH_3OH, CH_3CN, cyclohexane and H_2O (Table 1). The lower conversion was observed with CH_2Cl_2, CH_3OH, CH_3CN and H_2O. Again poor yield of product was observed in the case of cyclohexane. On the other hand, an excellent conversion was observed by considering (1:1) mixture of CH_2Cl_2/CH_3OH as a solvent (entry 7). Thus, by analyzing the results, the mixture of CH_2Cl_2/CH_3OH was used as a solvent for the current reaction.

Then to find the best reaction condition to accomplish the following oxidation reaction, the influence of the temperature on the catalytic activity of $FeCo_2O_4$

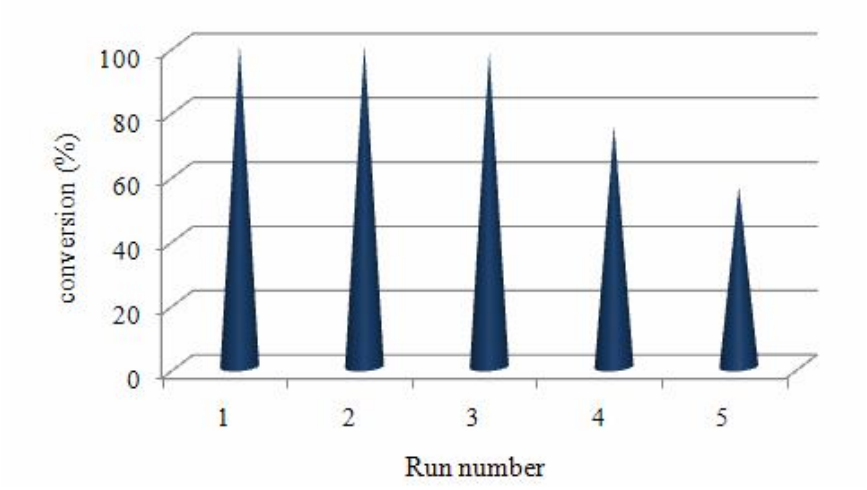


Fig. 5. Recycling studies of the $FeCo_2O_4$ nanoparticles in the oxidation of MPS.

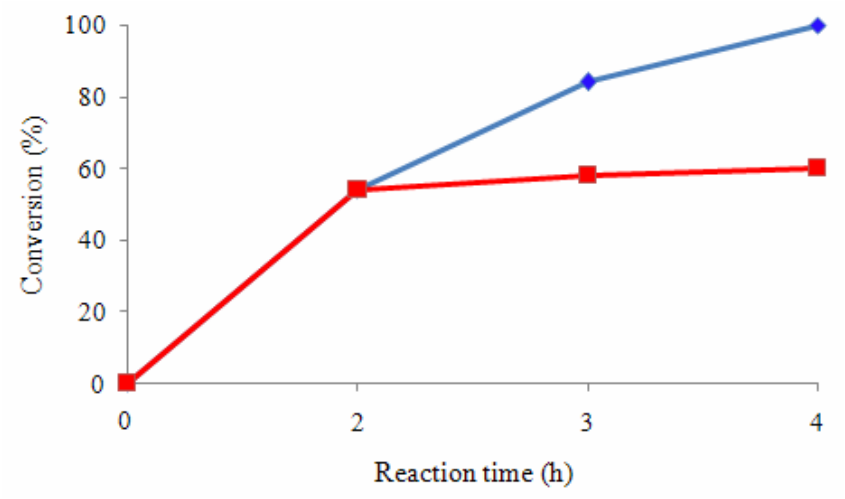


Fig. 6. Hot filtration test of the $FeCo_2O_4$ nanoparticles in the oxidation of MPS; red line: after filtration of catalyst.

nanoparticles was examined. As seen in Table 1, when the reaction was carried out at room temperature, the conversion of MPS was 48%, but at 30 °C, the conversion was improved to 85%. A temperature of 40 °C was required to get a full conversion of MPS with 90% selectivity (entry 5). However, if the reaction temperature reaches to 50 °C, selectivity decreases to 85%. Further, the oxidation reaction of MPS was carried out at different reaction times to find the best reaction time (entries 12-14). It can be seen that the complete conversion with high selectivity is achieved after 4 h (entry 14).

The as-prepared $FeCo_2O_4$ nanoparticles behave as a good sulfoxidation catalyst. The catalytic efficiency of as-prepared $FeCo_2O_4$ nanoparticles in the presence of various sulfide substrates is recorded in Table 2. A comparative catalytic study has been performed taking methylphenyl-sulfide, ethylphenylsulfide, benzyl phenyl sulfide, dibenzyl-sulfide, diphenylsulfide and diethyl sulfide as substrates using UHP as an oxidant. The very good conversions (69-100%) and selectivities (89-99%) depending on the nature of the sulfide substrates were obtained for all cases. In the substrates containing the benzylic C-H bonds such as benzyl

phenyl sulfide and dibenzylsulfide, no over oxidation was observed (entries 4 and 5). Oxidation of diethyl sulfide as an aliphatic substrate showed the lowest conversion and the highest selectivity as compared to other substrates.

Remarkable, $FeCo_2O_4$ nanoparticles in the reaction mixture under the oxidation condition were stable and therefore could be separated and reused easily after each treatment. After completing the first run of reaction, the mixture of the reaction was centrifuged and another run was done by the same nanoparticles. As shown in Fig. 5, the catalyst preserved its activity after the forth runs of recycling and MPS conversion did not change significantly.

To know that the $FeCo_2O_4$ nanoparticles are a real heterogeneous catalyst, hot filtration test was studied (Fig. 6). During this test, the $FeCo_2O_4$ nanoparticles were removed from the oxidation reaction after 2 h by filtration using a hot frit, and the filtrate was monitored for continued activity. The results show that after removal of the $FeCo_2O_4$ catalyst particles, the reaction did not proceed, indicating that no catalytically active $FeCo_2O_4$ nanoparticles remained in the filtrate and it's leaching is negligible throughout the oxidation process.

CONCLUSIONS

In conclusion, spinel-structured $FeCo_2O_4$ nanoparticles were prepared by annealing a Fe-Co precursor in the air at 350 °C. As-obtained $FeCo_2O_4$ nanoparticles were used as an efficient catalyst for the oxidation of sulfides. In the presence of $FeCo_2O_4$ nanoparticles, all of the substrates show satisfactory reactivity and corresponding sulfoxides could be furnished in relatively high yields. To best of our knowledge, this work is the first study of $FeCo_2O_4$ nanoparticles catalyzed the oxidation of sulfides.

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