

Dodecatungstocobaltate supported over ZSM-5 zeolite as novel solid catalyst in selective sulfide oxidation

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Abstract

The catalytic behavior of a Keggin type potassium dodecatungstocobaltate (II) salt supported on ZSM-5 zeolite for wet peroxide oxidation of 2-(methylthio)benzothiazole as a model organic sulfide was thoroughly studied. The Keggin salt was incorporated in the MFI zeolite matrix by the wet impregnation method followed by calcination at 350 °C. Catalysts were further characterized by XRD, UV-vis DR spectroscopy and SEM-EDAX techniques. Reaction parameters (nature of the solvent, hydrogen peroxide concentration, reaction time, catalyst mass, substrate initial concentration and reaction temperature) were evaluated to reach the optimum reaction conditions. Catalyst stability in several oxidation cycles was also examined.

Introduction

Sulfoxidation reactions have significant importance in organic chemistry, medicinal chemistry and drug metabolism. Sulfoxides, sulfones and other organosulfur

compounds are important synthetic intermediates in organic chemistry and are valuable in the preparation of biologically, medically and pharmaceutically relevant materials[1]. Organic sulfoxides and sulfones are extensively used as anti-ulcer, antibacterial, antifungal, antiatherosclerotic, antihypertensive, anthelmintic and cardiogenic agents, psychotropics, vasodilators and as central nervous system stimulants [2].

The most widely used method for the preparation of sulfoxides and sulfones is the oxidation of the corresponding sulfide. For this reason, sulfide oxidation to sulfoxides and sulfones has been the subject of many studies, and several methods for this transformation have been reported in the literature [3]. Traditionally, selective oxidation of sulfides to sulfoxides and sulfones is achieved using stoichiometric amounts of organic and inorganic reagents and the most common problems encountered during the reaction is the formation of copious amounts of toxic wastes and over oxidation products [4].

From an ecological standpoint, the exclusion of pollutants from unselective preparation methods is always preferable to subsequent treatment. In this context, the goal of modern organic synthesis is to develop efficient catalytic methods that can produce compounds with atom economy and environmental advantages. Considering oxidation reactions with oxygen donors, one of the preferred methods is based on catalytic oxygen transfer from clean oxygen donors, such as hydrogen peroxide [5, 6]. Aqueous 30 % hydrogen peroxide has been used as an attractive and environmental friendly oxidant for the oxidation of sulfides, because it is inexpensive, safely stored and produces only water as by-product. Since the oxidation of sulfides with aqueous hydrogen peroxide in the absence of any catalyst is slow, several transition metal compounds have been used as catalysts for this reaction [7].

Catalysis offers relevant possibilities for sustainable production. The replacement of environmental hazardous catalysts in existing processes, as that related to the use of solid catalysts as alternative to homogeneous processes, is one of the innovative trends. In this context, the use of catalytic processes with Keggin type heteropolycompounds (HPC) has been widely studied in recent decades. One of the reasons is related to the dual character of such compounds, since they are strong acids and can also act as efficient oxidants. Therefore, it appears to be an interesting challenge to obtain new catalysts based on heteropolycompounds for this type of reactions [8, 9].

However, the low surface area (typically $1\text{--}10\text{ m}^2\text{ g}^{-1}$) and porosity (lower than $0.1\text{ cm}^3\text{ g}^{-1}$) of bulk HPC, together with a high solubility in polar solvents, lead to the search of supports that can properly immobilize them [10, 11]. In this sense, the heterogenization or immobilization of homogeneous complexes on high surface area supports has developed as a promising strategy for combining the advantages of homogeneous and heterogeneous catalysts due to their easy separation from the products by filtration and the possibility of recycling them by continuous operation [7]. For this purpose, the use of zeolites as highly ordered and with an unusual high surface area seems to be an interesting alternative as support of the HPC. Zeolites represent the most important group of industrial heterogeneous catalysts with large-scale applications in refining and petrochemistry and increasing potential in environmental catalysis and synthesis of fine chemicals. Zeolites are crystalline microporous aluminosilicates offering a plethora of modifications and opportunities for further improvement of their properties. The possibility to control the textural properties together with adjustable acidity (type, concentration and strength of acid sites) is the most important feature of zeolites [12].

In order to make a deep study of the influence of the catalyst and reaction parameters in organic sulfide selective oxidations, 2-(methylthio)benzothiazole was chosen as model substrate. The main goal of this paper is to evaluate the possibility of using a polioxotungstocobaltate with Keggin structure supported on ZSM-5 synthetic zeolite as solid catalyst for the liquid phase oxidation of 2-(methylthio)benzothiazole.

2. Experimental

2.1 Catalysts preparation

The hydrothermal crystallization method was employed to synthesize ZSM-5 zeolite (Si/Al=17) in the Na₂O-Al₂O₃-SiO₂ system, using TPAOH (Tetrapropylammonium Hydroxide) as a structure directing agent by known methods [13]. The obtained gel reached a pH > 9 and was maintained at 120-160 °C for 10 days under self-generated pressure on autoclave. Afterwards, the reaction product was extracted, washed and dried at 110 °C for 12 h. The structure directing agent (TPA) was desorbed in N₂ atmosphere (20 ml/min) at programmed temperature (10 °C/min) from room temperature to 500 °C and then it was calcined in air at 500 °C for 12 h to obtain Na-HZSM-5.

The ammonium form of the zeolite was obtained after ion-exchange of Na-zeolite with NH₄Cl (1 M) for 40 h at 80°C. In order to obtain H-ZSM-5 the NH₄-ZSM-5 was desorbed for 16 h in N₂ (10 ml/min) at 500°C and later calcined in air at 500°C for 8 h.

The synthesis of the potassium dodecatungstocobaltate (II) salt K₆[CoW₁₂O₄₀].6H₂O (from now on named CoW₁₂) was adapted from that reported by Baker and McCutcheon [14] taking into account the modifications made by Nolan et al.

[15]. It was characterized by FT-IR and the purity was checked spectrophotometrically [16].

For CoW₁₂-ZSM-5 samples, wet impregnation method was employed. NH₄-ZSM-5 was used as starter matrix and 35 wt% of CoW₁₂ salt (1 wt% of cobalt) was deposited over the zeolite. Water was evaporated using a rotator–evaporator at 80°C under vacuum until complete dryness. Afterwards, samples were dried at 110°C and treated under N₂ flow at 350°C for 12 h, followed by calcination in air at 350 °C for 8 h to obtain the final material .

2.2 Catalysts characterization

Structure and cristallinity of the samples were studied by X-ray diffraction patterns collected in air at room temperature in a Philips diffractometer using CuK α radiation. Diffraction data were recorded between $2\theta = 5^\circ$ and 60° at an interval of 0.05° . A scanning speed of $2^\circ/\text{min}$ was used.

Chemical composition was determined by using an inductively coupled plasma emission spectrophotometer Varian 715ES.

The morphological features and texture of supported and unsupported catalysts were obtained using scanning electron microscopy (SEM) in a Philips 505 microscope at 14-20Kv accelerating voltage using fine catalyst powder supported on carbon tape an over aluminum tip and coated with gold.

The distribution of CoW₁₂ over the ZSM-5 matrix was measured using a Philips Model 505 scanning electron microscope with energy dispersive X-ray analysis (EDAX) system. The secondary electron micrographs of selected solid samples were obtained.

2.3 Catalytic activity

Catalytic selective oxidation of 2-(methylthio)benzothiazole (97 %, Aldrich) with H₂O₂ (aqueous solution 30 wt%, Cicarelli) as oxidant agent was carried out in a glass flask reactor (25 cm³) with magnetic stirring immersed in a thermostated bath, equipped with a reflux condenser. The catalytic tests were performed from room temperature to 60°C, evaluating different reaction conditions such as catalyst mass and different molar ratios of sulfide/hydrogen peroxide (R). Several solvents with different dielectric constants were tested for the reaction: acetonitrile (99.5 % Cicarelli), acetone (analytical grade, Aldrich), 2-propanol (99.5 %, Aldrich), methanol (99.5%, Cicarelli), ethanol (99.5%, Cicarelli), 2-butanol (99.5%, Merck) and n-hexane (97%, Riedel de Haën). The reaction was monitored by taking aliquots of the reaction mixture at different reaction times. Prior to analysis, the catalyst was separated by filtration. Organic compounds were analyzed quantitatively by gas chromatography (Hewlett Packard HP-5890) with a Methyl Silicone capillary column (30m x 0.32 mm id) and a flame ionization detector (FID), and qualitatively, by mass spectrometry GC- Mass (Shimadzu QP 5050 GC-17 A), using a HP-S (25 m x 0.2 mm i.d) capillary column. The substrate conversion was measured as a function of reaction time and the values observed are reported as mol %.

3. Results and Discussion

3.1. Catalyst characterization

It was previously reported [10] that according with the FT-IR results the structure of the [CoW₁₂O₄₀]⁶⁻ anion was preserved after the impregnation of the ZSM-5 and the thermal treatment of the final material. The FT-IR spectrum of CoW₁₂-ZSM-5 showed the characteristic bands of the [CoW₁₂O₄₀]⁶⁻ anion at 941, 873 and 762 cm⁻¹,

assigned to the stretching vibrations W_{Od} , W_{Ob} , and W_{Oc} , respectively overlapped to those of the zeolite.

The XRD pattern of the CoW_{12} -ZSM-5 sample (Figure 1) displays the characteristic peaks of ZSM-5 zeolite. The characteristics of XRD pattern of the sample CoW_{12} -ZSM-5 was similar to that of the zeolite, so neither the diffraction lines of CoW_{12} , nor those of other crystalline phases were detected. From these results it can be inferred that the $[CoW_{12}O_{40}]^{6-}$ species present onto the support surface are highly dispersed as a non-crystalline form

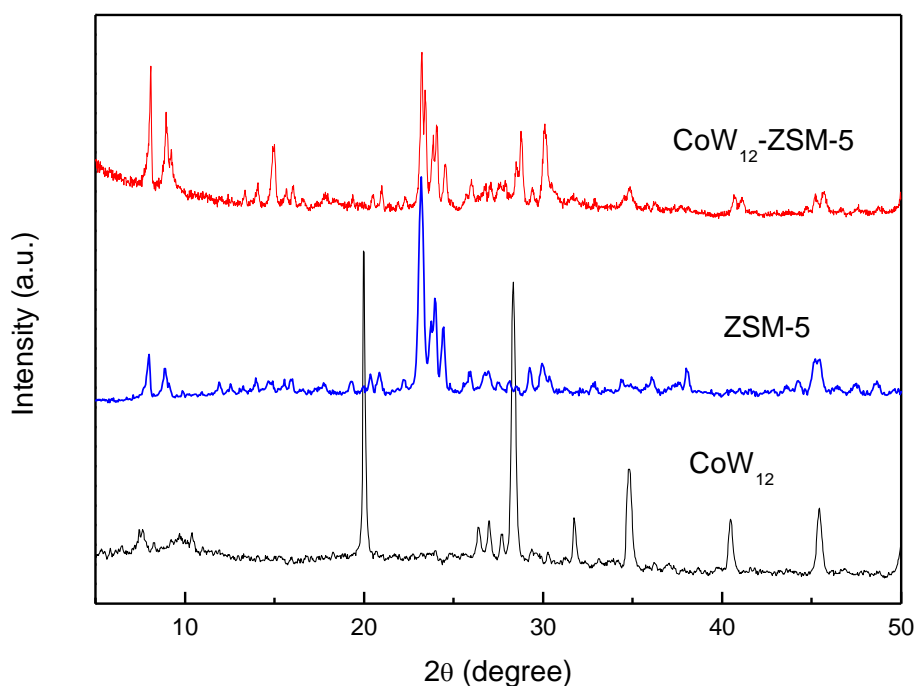


Figure 1. Diffraction patterns of samples CoW_{12} , ZSM-5 and CoW_{12} -ZSM-5.

In order to check the crystalline formation and dispersion of CoW_{12} over ZSM-5 zeolite, scanning electron micrographs (SEM) were taken (Figure 2). The blocky faceted grains are parallelepipeds with edges of approximately 300 nm and correspond to the zeolite matrix.

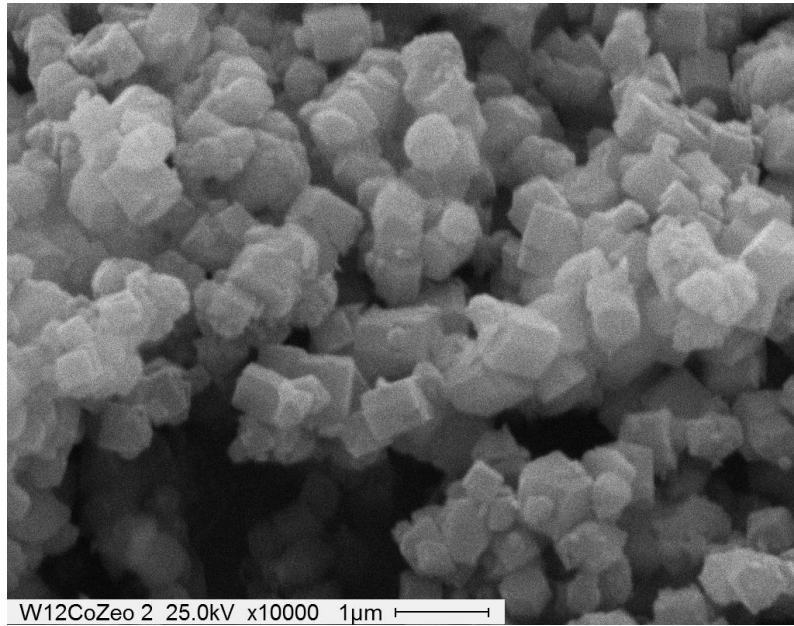


Figure 2. Micrography of CoW₁₂-ZSM-5 taken at 10000x

The EDS analysis spectrum of the surface is shown in Figure 3. In the spectra, the characteristic peaks corresponding to the matrix (0.5, 1.1, 1.5 and 1.9 keV) are seen and the signals corresponding to CoW₁₂ (0.5, 3.4, 6.9 and 8.4 keV) anion are also present. From EDS spectrum, Si/Al ratio is 16.8, in accordance with the theoretical estimation (17) and ICP result (17.8).

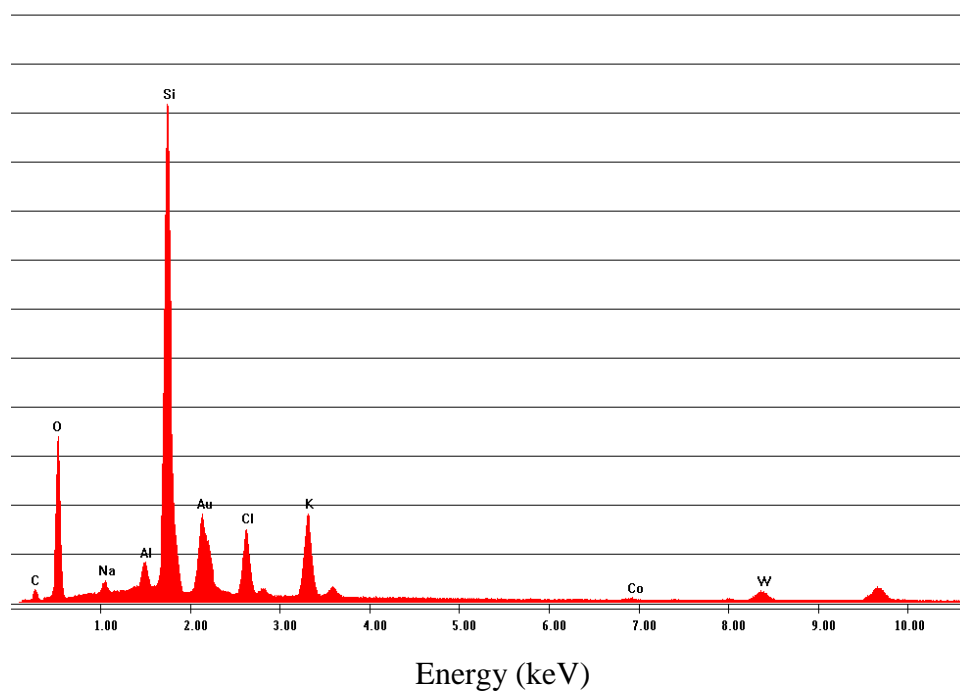


Figure 3. EDS spectra of CoW₁₂-ZSM-5 sample.

These results showed a uniform distribution of CoW₁₂ in the external surface of CoW₁₂-ZSM-5 sample

3.2. Sulfide oxidation

The results of 2-(methylthio)benzothiazole (2MTBT) oxidation employing hydrogen peroxide as oxidant and acetonitrile as solvent over CoW₁₂, H-ZSM-5 and CoW₁₂-ZSM-5, are given in Figure 4. CoW₁₂-ZSM-5 is the most active catalyst of all the samples evaluated for this reaction, being the corresponding sulfoxide and sulfone the only products obtained. Even when the bulk form of the heteropolycompound (CoW₁₂) and the zeolite matrix (H-ZSM-5) are active for the oxidation, supported CoW₁₂ over the MFI zeolite (CoW₁₂-ZSM-5), seem to be quite more active than them.

Specially when considering that in all the cases 0.1 g of each catalyst was employed and in the case of CoW_{12} -ZSM-5 it just contains 35 %p/p of the polyoxotungstocobaltate.

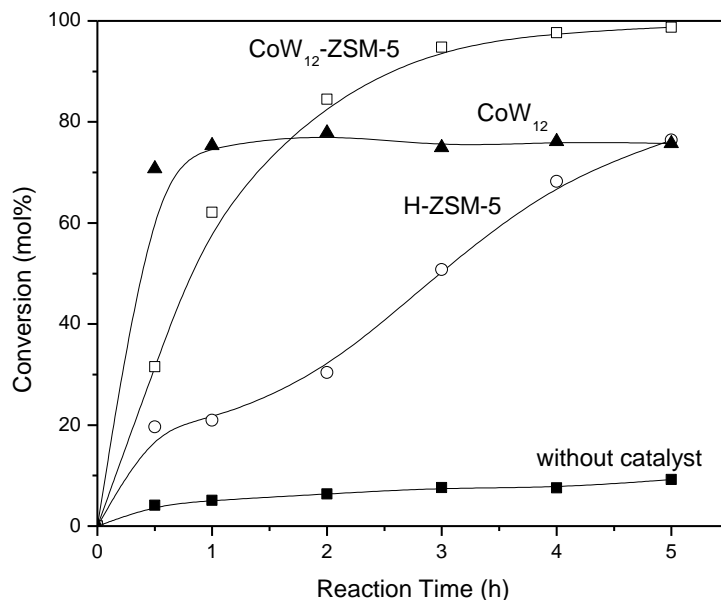


Figure 4. 2MTBT oxidation over different cobalt catalysts. Reaction conditions: 0.1 g of catalyst; acetonitrile as solvent; Temperature: 40 °C; R.

When H-ZSM-5 was used as catalyst for the oxidation, sulfide conversion increases with reaction time reaching a 76 mol% after 5 hours of reaction. In the case of the bulk CoW_{12} as catalyst, a plateau of 75 mol% in the sulfide conversion was obtained after the first reaction hour, while when employing the supported counterpart, a 99 mol% was reached after the fourth hour of reaction.

Products distribution was quiet similar for the three catalysts, even though, the highest selectivity to the sulfone was reached when CoW_{12} -ZSM-5 was used. So, we could conclude that CoW_{12} supported on ZSM-5 was the optimal material for this catalytic reaction.

We found in a previous paper [10], for 2,3,5-trimethylphenol oxidation under this supported CoW_{12} , that the dispersion of the heteropolycompound over the zeolite

matrix, increased the exposure area of the CoW_{12} , which seems to be the most active component of the catalyst, favouring substrate-active sites-oxidant contact. This observation is valid for this new reaction system according with the results presented in Figure 4.

When the reaction was done without the presence of a catalyst, just a 9 mol% of sulfide conversion was obtained. This result confirms the necessary activation of the oxidant by the catalyst.

To gain insight the reaction mechanism, the evolution of the sulfide conversion and sulfoxide and sulfone selectivities as function of the reaction time are plotted in Figure 5. It is possible to observe that while 2MTBT conversion increases with reaction time, sulfoxide selectivity decreases and sulfone's yield is benefited. This observation is in agreement with the reaction mechanism presented in Scheme 1. **If further oxidant is added, sulfoxide would be converted in sulfone.**

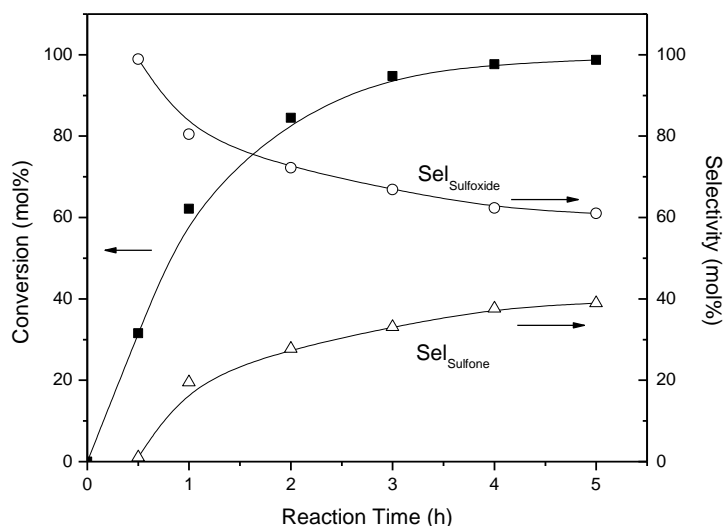
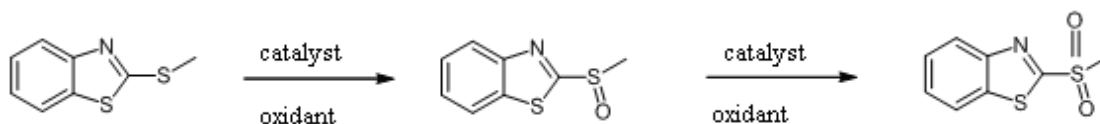


Figure 5. Reaction evolution as time function. Reaction conditions: 0.1 g CoW_{12} -ZSM-5, H_2O_2 as oxidant, Acetonitrile as solvent, 40 °C.



Scheme 1. 2MTBT oxidation pathway.

We found that neither the sulfur atom, nor the nitrogen of the thiazole ring were affected under the conditions employed in this reaction, in agreement with the results published by Kinen et al [17] using an homogeneous catalytic system and employing $\text{Fe}(\text{NO}_3)_3$ as oxidant.

3.3. Factors influencing the catalytic activity of $\text{CoW}_{12}\text{-ZSM-5}$

For any catalytic system, the choice of reaction conditions and the stoichiometry of H_2O_2 with respect to the catalyst and substrate are critical parameters to the yields of the reaction [18]. Thus why, the effect of different reaction parameters were studied employing $\text{CoW}_{12}\text{-ZSM-5}$ as solid catalyst.

The influence of the catalyst mass in the 2MTBT oxidation is illustrated in Figure 6. Catalyst incorporation in the reaction system produces a remarkable increment in sulfide conversion, which goes from 9 to 95 mol%. Sulfide conversion, after 5 h of reaction, grew from 95 to 99 mol%, when the amount of $\text{CoW}_{12}\text{-ZSM-5}$ was increased from 0.05 to 0.1 g, while sulfoxide selectivity presented a decreasing trend.

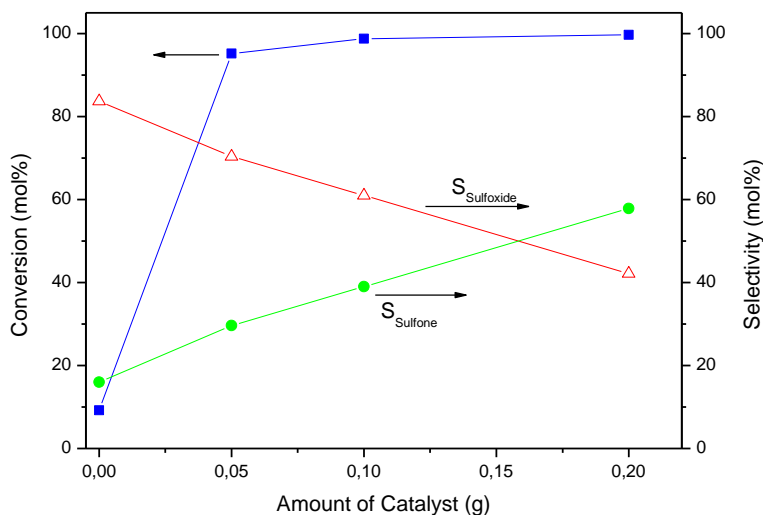


Figure 6. Effect of the mass of CoW_{12} -ZSM-5 in 2MTBT oxidation after 5 h. Reaction conditions: H_2O_2 as oxidant, Acetonitrile as solvent, $40\text{ }^\circ\text{C}$, $R = 0.1$.

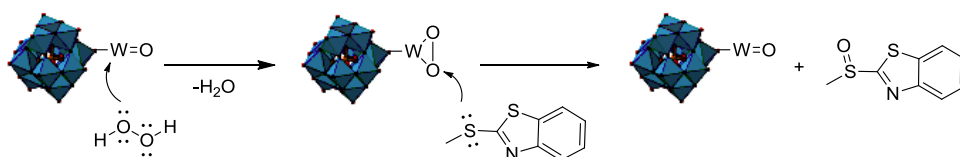
When studying diphenyl sulfide oxidation over Mo-based Keggin heteropolyacids, Palermo et al. [19] suggested that the reactions goes through the formation of peroxy-molybdate species and the subsequent nucleophilic attack of the sulfur atom in the sulfide on the peroxy species. Meanwhile, Maciucă et al. proposed that the electrophilicity of the peroxide oxygen of H_2O_2 is increased by an oxometal group ($\text{M}=\text{O}$) in the heteropolycompound [20].

Considering these hypothesis and according to our results, we can suggest that the oxidation of 2-(methylthio)-benzothiazole to the corresponding sulfoxide and sulfone using H_2O_2 in the presence of CoW_{12} takes place by the mechanism showed in Scheme 2a and 2b. The interaction of hydrogen peroxide with the dodecatungstocobaltate anions generates an electrophilic intermediate (peroxy oxygen/metal), which produces an electrophilic attack to the sulfur atom in the sulfide, generating the corresponding sulfoxide (Scheme 2a).

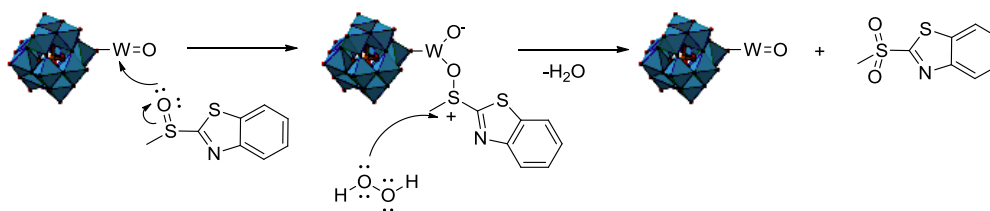
The mechanism for the oxidation of the sulfoxide to the corresponding sulfone is different. First it involves the formation of an CoW_{12} -sulfoxide intermediate through the nucleophilic attack to the tungsten atom in the dodecatungstocobaltate by the oxygen of the sulfoxide, and then the nucleophilic attack of the sulfur atom in HPC-sulfoxide by H_2O_2 via a $\text{S}_\text{N}2$ mechanism [21-23] (Scheme 2b).

If we consider CoW_{12} -sulfoxide intermediate formation as the slowest step of the sulfide oxidation, when catalyst mass is increased, it would be favoured. It also explained the increment of the amount of sulfoxide oxidation to the corresponding sulfone with the increment of catalyst mass.

a) 2-(methylthio)-benzothiazole oxidation to the corresponding sulfoxide



b) 2-(methylthio)-benzothiazole sulfoxide oxidation to the corresponding sulfone



Scheme 2. Suggested mechanism for the oxidation of 2-(methylthio)-benzothiazole to the corresponding sulfoxide and sulfone with aqueous hydrogen peroxide in the presence of polyoxometalates

Considering that sulfide conversion maximum using 0.1g of the catalyst was reached in a shorter time (3 h) than when 0.05 g were employed (5 h), and taking into

account that no significant increment of the conversion was obtained using 0.2 g, we selected 0.1 g of catalyst for further studies.

In order to determine the influence of the oxidant concentration on the sulfide oxidation, a series of tests were made varying the H₂O₂ initial concentration and keeping constant substrate (2 mmol) and catalyst (0.1 g) quantities. The effect in sulfide conversion and sulfoxide/sulfone selectivities are shown in Table 1.

Table 1. Effect of hydrogen peroxide initial concentration in the reaction progress

[H ₂ O ₂](M)	Conversion (mol%)	Selectivity _{Sulfoxide}	Selectivity _{Sulfone}
0	0	--	--
0.8	84	81	19
1.6	97	74	26
3.1	99	61	39
6.2	97	59	41

According to catalytic results, as oxidant initial concentration increases, sulfoxide selectivity decreases and sulfone concentration enhances. This observation is in consonance with the proposed reaction mechanism (Scheme 1) which involves a two step oxidation process. When more oxidant molecules are present in the reaction system for the same substrate concentration, the second step of the oxidation is favor.

When a radical scavenger (isopropyl alcohol) was added to the reaction solution, 2MTBT conversion and sulfoxide and sulfone yields were the same than those obtained without it. This result is a strong hint of the absence of a radical oxidation mechanism.

Figure 7 shows the effect of 2MTBT initial concentration in conversion and products selectivities. It is evident that when sulfide concentration increases regarding

to oxidant and catalyst concentration, sulfoxide yield increases reaching a maximum value of 76 mol%. This means that when a higher number of 2MTBT molecules are present, active sites availability diminishes and sulfone production is minimal. This fact could be used if sulfoxide production is desired, instead of sulfone.

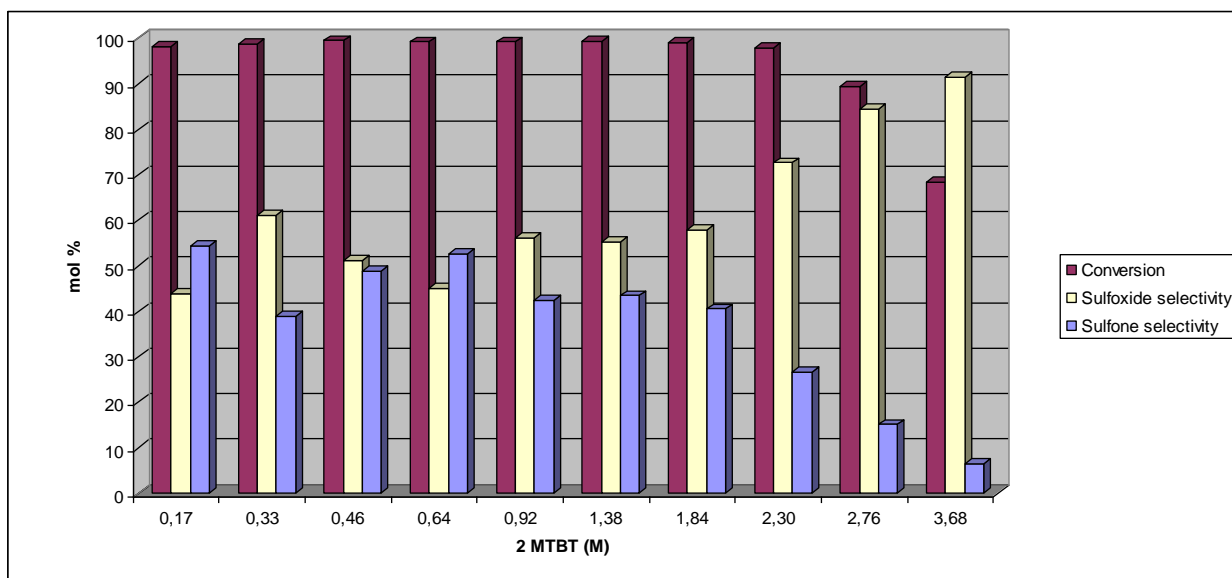


Figure 7. Products selectivities and 2MTBT conversion as function of its initial concentration. Reaction conditions: 0.0186 moles H_2O_2 , Acetonitrile as solvent, 40 °C, 5 h of reaction.

To avoid the formation of two liquid phases and the mass transfer problems associated with them, a group of different solvents was evaluated. It is a relevant study since the nature of the solvent has an important effect on the outcome of the reaction considering yields, by-products formation and reaction kinetics [24]. A series of solvents with different characteristics of polarity and proticity were tested for this oxidation. The influence of solvent selection on 2MTBT conversion and sulfoxide and sulfone selectivities is shown in Figure 8. As could be seen, solvent effect is not a key factor for this oxidation, since no significant changes were obtained when solvent was

varied from Acetonitrile (aprotic and polar solvent) to 2-Butanol (protic and less polar solvent). When employing Hexane (aprotic, non-polar) as solvent, ca. 30 mol% of reduction in sulfide conversion was obtained, possible due to the occurrence of phases separation that limit the accessibility of substrate and oxidant molecules to the active sites of the catalyst. In the case of Ethanol, the second step of the reaction was favored since the selectivity to the sulfone is the highest of the entire group.

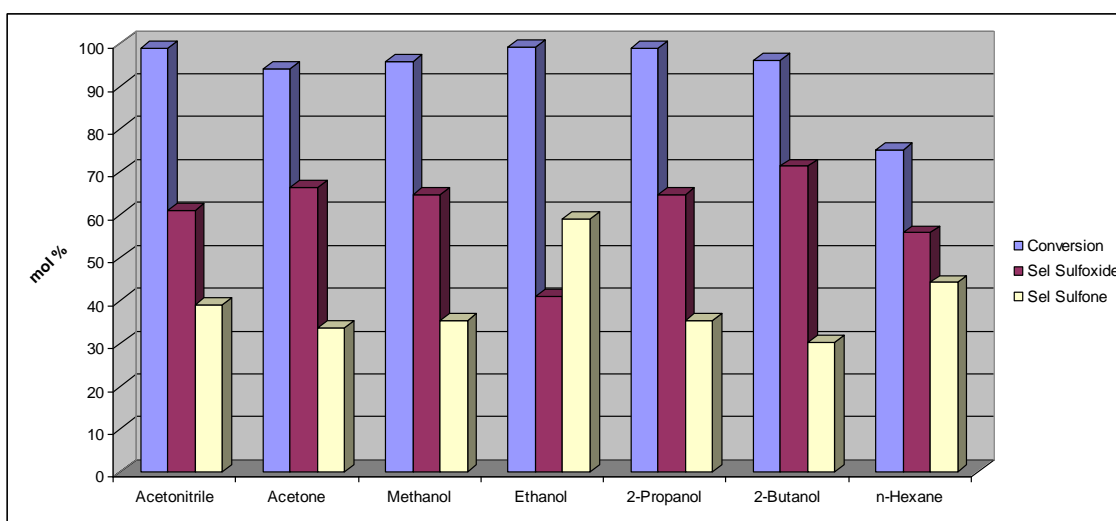


Figure 8. Solvent effect in 2MTBT oxidation. Reaction conditions: H_2O_2 as oxidant, 40 °C, $R= 0.1$, 5 h of reaction.

Temperature influence in the evolution of the reaction was also evaluated and the results are presented in Figure 9. It is noticeable that when temperature was varied between room temperature and 40 °C, sulfide conversion grew from 78 to 99 mol%, while products selectivities remained almost constant. When reaction temperature, was elevated to 50 °C, sulfide conversion maintained a constant value, but sulfoxide selectivity suffered a sharp decrease while sulfone yield was noticeable favoured. This result is in agreement with the fact that CoW_{12} -sulfoxide intermediate formation is the slowest step of the sulfide oxidation (higher activation energy). So, when temperature was increased, it would be favoured.

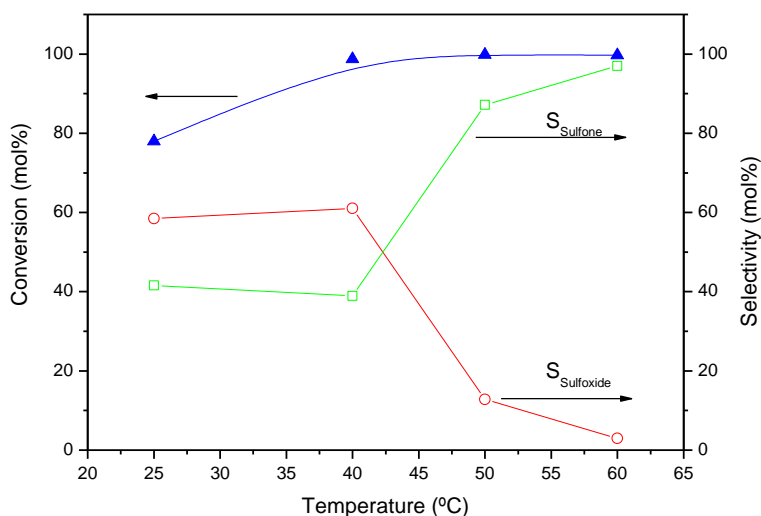


Figure 9. Influence of reaction temperature. Reaction conditions: H₂O₂ as oxidant, 5 h of reaction time, acetonitrile as solvent, CoW₁₂-ZSM-5 0.1 g, R= 0.1

3.4. Catalyst stability

In order to determine the stability of CoW₁₂-ZSM-5 catalytic properties, its catalytic performance was studied in a number of successive cycles for sulfide oxidation. Several problems could cause catalyst deactivation (leaching of the active species, blockage of the active sites by absorption of reactive molecules, structure collapse, etc) and it is necessary to avoid them. The employed protocol for this study consists in separate the solid catalyst after the reaction was finished and then calcined at 350 °C for 6 h. In table 2 are presented catalytic results after 5h of reaction employing Acetonitrile as solvent, 40°C and 0.1 molar ratio of 2MTBT:H₂O₂ in the successive reaction cycles.

Table 2. CoW₁₂-ZSM-5 stability in successive 2MTBT oxidation cycles

Number of cycle	Conversion (mol%)	S _{sulfoxide} (mol%)	S _{sulfone} (mol%)
1	99	10	90
2	100	11	89
3	100	12	88
4	100	11	89

According to these results, CoW₁₂-ZSM-5 is a stable catalyst for sulfide oxidation in aqueous media. Both conversion and selectivities to sulfoxide and sulfone remained almost unchanged after several catalytic uses, showing that CoW₁₂-ZSM-5 is an effective solid catalyst for this purpose.

Conclusions

According to the results obtained, it is possible to consider supported CoW₁₂ over ZSM-5 zeolite as an efficient and stable catalyst for 2-(methylthio)-benzothiazole oxidation by wet hydrogen peroxide. High yields of the corresponding sulfoxide and sulfone were obtained employing mild conditions in the presence of this heterogeneous catalyst. Therefore, it is possible to recover and reuse the catalyst for several reaction cycles without considerable loss of activity.

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