

2,3,5-Trimethylphenol oxidation over Co-based solid catalysts



Clara Saux^{a,c,*}, Luis R. Pizzio^{b,c}, Liliana B. Pierella^{a,c}

^a Grupo Zeolitas – CITEQ (Centro de Investigación y Tecnología Química), Facultad Regional Córdoba, Universidad Tecnológica Nacional, Maestro Lopez y Cruz Roja Argentina, 5016 Córdoba, Argentina

^b Centro de Investigación y Desarrollo en Ciencias Aplicadas “Dr. J.J. Ronco” (CINDECA), Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT La Plata, CONICET, 47 No. 257, 1900 La Plata, Argentina

^c CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), Argentina

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ABSTRACT

2,3,5-Trimethylphenol (TMP) was oxidized with hydrogen peroxide employing cobalt based solid materials. $K_6[\text{CoW}_{12}\text{O}_{40}]\cdot 6\text{H}_2\text{O}$ (CoW_{12}) was probed as selective catalyst for the oxidation obtaining better results when it was supported over ZSM-5 zeolites (CoW_{12} -ZSM-5). CoW_{12} -ZSM-5 was found to be an efficient catalyst in the oxidation of TMP to 2,3,5-trimethylbenzoquinone (TMBQ) and 2,3,5-trimethylhydroquinone (TMHQ) under mild reaction conditions. Liquid phase reaction parameters were evaluated obtaining better results employing hydrogen peroxide as oxidant, with an oxidant/substrate molar ratio of 5, methanol as solvent and 60 °C as reaction temperature. An apparent activation energy of 94.19 kJ/mol was obtained.

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1. Introduction

The selective catalytic oxidation of organic compounds using environmentally friendly and cheap oxidants, such as aqueous H_2O_2 , and easily recyclable heterogeneous catalysts is a challenging goal of fine chemistry [1]. Heterogeneous catalysis is generally considered to be an effective method for oxidation reactions. One of its major advantages is the facile separation and recovery of catalyst without tedious experimental workup. These advantages together with the absence of wash water containing the dead catalyst may lower the production costs [2,3].

The new green legislations call for the lowering of waste production and the use of more friendly alternative reagents and catalysts. This goal can be achieved through the application of the principles of green chemistry that provide a framework for designing more eco-compatible routes to fine chemical production [4]. Heterogeneous catalysis suites good these demands, as it appears as a selective and easily recyclable method.

Oxidation of phenols to quinones has been the subject of many studies and it is of industrial interest because various quinones are used as intermediates in the synthesis of fine organic materials such as drugs, vitamins and perfume aromas [5].

TMBQ is one of the most important intermediates for production of vitamin E (α -tocopherol). First, TMBQ is reduced to TMHQ and then it reacts with isophytol to obtain the α -tocopherol as proposed by Mercier and Chabardes [6]. Because it functions as anti-free radical, which provides the effect of preventing aging, apoplexy, heart disease, cardiovascular vessel disease and cancer, vitamin E is one of the most important vitamins nowadays and is used extensively as antioxidant in food, medical treatments and cosmetics [7]. Nowadays, the demand reaches several millions pounds every year. The reason that vitamin E is so expensive is that the TMBQ is difficult to produce on a large scale. Therefore, in the recent years many scientists devote themselves to study the way of how to achieve mass production, that is fast, effective and at low cost for producing TMBQ [8,9].

The traditional procedure for producing TMBQ involves sulfonation, oxidation and reduction from TMP. The sulfonation of TMP with sulfuric acid produces 4-hydroxytrimethylbenzenesulfonic acid; the oxidation of the 4-hydroxytrimethylbenzenesulfonic acid by oxidants, such as MnO_2 gives TMBQ. In the end, the reduction of TMBQ by hydrogen produces the final product of TMHQ. This procedure generally generates a great amount of solid and liquid wastes because of the use of sulfuric acid and stoichiometric

* Corresponding author at: Grupo Zeolitas – CITEQ (Centro de Investigación y Tecnología Química), Facultad Regional Córdoba, Universidad Tecnológica Nacional, Maestro Lopez y Cruz Roja Argentina, 5016 Córdoba, Argentina.
Tel.: +54 351 4690585; fax: +54 351 4690585.

E-mail addresses: csaux@scdt.frc.utn.edu.ar, csaux@hotmail.com, clarasaux@gmail.com (C. Saux).

solid oxidants and reductants [10–12]. So, the development of environmentally friendly catalytic methods in last years has become a promising advance in this way. So far, several protocols have been established for the direct oxidation of TMP to TMBQ, however only few of them are of industrial relevance [7]. Liu et al. [8] showed that copper ferrite nanopowders were good catalysts for 2,3,6-trimethylphenol oxidation, but the procedure includes hydrochloric acid incorporation with its well-known corrosive effect.

Kholdeeva et al. [13] described the use of molybdovanadophosphoric heteropolyacid (HPA) for the selective oxidation of TMP to TMBQ but in a homogeneous system. Even when catalytic results were promising it was still present the catalyst separation problems. So, the use of HPA supported catalysts appears as a promising alternative to reach heterogeneous reaction systems. The catalytic properties of heteropolycompounds (HPC) have drawn much attention in the last decades owing to the versatility of these compounds as catalysts, which has been demonstrated both by promising laboratory results and successful industrial applications [14,15]. The Keggin-type heteropolycompounds are well known as oxidation and acid catalysts in which the acid-based and redox properties can be tuned by variation of the central heteroatom (X) and the addenda (M) atoms [16].

The general formula for the heteropolyanions with Keggin-type structure is $[XM_{12}O_{40}]^{(8-n)-}$, where M is usually W or Mo and X is P, Si or Co, being the oxidation state of X. This is a well-known structure consisting of a central tetrahedron XO_4 surrounded by twelve octahedra MO_6 arranged in four groups of three edge-sharing octahedra, which are linked by corners. Such compounds show high catalytic activity both for acid–base and redox reactions [17].

HPC are reversibly acting oxidants widely used as a mediator system for liquid phase oxidations [13]. Also, the HPC have other special properties, which are very useful in catalysis, such as high solubility in water and organic solvents, and a moderately high thermal stability in solid state. All these properties make possible the use of HPC both in homogeneous and heterogeneous catalysis.

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 [18,19], together with a high solubility in polar solvents, lead to the search of supports that can properly immobilize them. The catalytic activity of the immobilized HPC strongly depends on the support properties, the HPC concentration, and the pretreatment conditions to which the material is subjected [20]. Basic solids such as Al_2O_3 tend to decompose HPC [21,22]. Acidic or neutral substances such as SiO_2 , active carbon, or ZrO_2 [22–24] were reported as suitable supports. Having in mind the acid nature of ZSM-5 zeolites, we may assume they are suitable HPC supports.

Their crystalline structure provides access to very large and well-defined surfaces with uniform pore structures which can act as a convenient compartment for HPC or metal cations deposition.

Cobalt-containing zeolites have drawn a great deal of attention in recent years. These materials may contain at least two different kinds of cobalt species in cationic ion-exchange positions in ZSM-5 and cobalt oxide particles in the zeolite channels or over the external surface of the zeolite microcrystals when the samples are heated in an oxidant atmosphere. These cobalt species may exhibit interesting catalytic behavior in oxidation reactions [25].

In this paper, we propose and discuss the use of supported $K_6[CoW_{12}O_{40}]\cdot 6H_2O$ (CoW_{12}) with Keggin structure over ZSM-5 zeolites as active and selective solid catalysts for the production of TMBQ and TMHQ from the oxidation of TMP using aqueous hydrogen peroxide as oxidant and their comparison with other traditional metal-zeolites, such as Co-ZSM-5.

2. Experimental

2.1. Catalysts preparation

ZSM-5 zeolite ($Si/Al=17$) was obtained by hydrothermal crystallization in the $Na_2O\text{--}Al_2O_3\text{--}SiO_2$ system, using TPAOH (tetrapropylammonium hydroxide, Fluka) as a structure directing agent by known methods [26] with some modifications made by our group. Aqueous solution of sodium aluminate was introduced into a Si_2O solution which was prepared previously by partial dissolution on TPAOH aqueous solution. The obtained gel reached a $pH > 9$ and was maintained at $120\text{--}160\text{ }^\circ\text{C}$ for 10 days under self-generated pressure on autoclave. Afterwards, the reaction product was extracted, washed and dried at $110\text{ }^\circ\text{C}$ for 12 h. The structure directing agent (TPA) was desorbed in N_2 atmosphere (20 ml/min) at programmed temperature ($10\text{ }^\circ\text{C/min}$) from room temperature to $500\text{ }^\circ\text{C}$ for 8 h and then it was calcined in air at $500\text{ }^\circ\text{C}$ for 12 h to obtain Na-ZSM-5. The ammonium form of the catalyst ($NH_4\text{-ZSM-5}$) was prepared by ion-exchange of Na-zeolite with NH_4Cl (Fluka, 1 M) for 40 h at $80\text{ }^\circ\text{C}$ in a batch reactor with continuous mechanical agitation. To prepare H-ZSM-5, the ammonium form was desorbed for 8 h in N_2 (10 ml/min) at $500\text{ }^\circ\text{C}$ and later calcined in air at $500\text{ }^\circ\text{C}$ for 8 h.

In order to obtain Co-ZSM-5, the ammonium form was suspended in a solution of $CoCl_2\cdot 6H_2O$ (Fluka) in the least amount of distilled water in order to obtain a 1 wt%. Water was evaporated using a rotator-evaporator at $80\text{ }^\circ\text{C}$ under vacuum until complete dryness. After that, the samples were dried at $110\text{ }^\circ\text{C}$ and desorbed in N_2 flow (10 ml/min) at programmed temperature ($10\text{ }^\circ\text{C/min}$) from room temperature to $500\text{ }^\circ\text{C}$ for 12 h followed by calcination in air at $500\text{ }^\circ\text{C}$ for 12 h.

The synthesis of the potassium dodecatungstocobaltate (II) salt $K_6[CoW_{12}O_{40}]\cdot 6H_2O$ (from now on named CoW_{12}) was adapted from that reported by Baker and McCutcheon [27] taking into account the modifications made by Nolan et al. [28]. It was characterized by FT-IR and the purity was checked spectrophotometrically [29].

For $CoW_{12}\text{-ZSM-5}$ samples, wet impregnation method was employed, as in the case of Co-ZSM-5 catalyst. $NH_4\text{-ZSM-5}$ was used as starter matrix and 1 wt% of cobalt was deposited over ZSM-5 matrix. Afterwards, samples were dried at $110\text{ }^\circ\text{C}$ and treated under N_2 flow at $350\text{ }^\circ\text{C}$ for 12 h, followed by calcination in air at $350\text{ }^\circ\text{C}$ for 8 h to obtain the final material.

2.2. Catalysts characterization

The metal effective percentage of all the samples under study was determined by Atomic Absorption in a Perkin Elmer AAnalyst 800 spectrometer after the digestion of the samples by microwave in a Milestone ETHOS 900 digester. BET surface area determinations were carried out with an ASAP 2000 equipment. Crystal structure determinations were performed by means of X-ray diffraction patterns collected in air at room temperature in a Philips diffractometer using $Cu\ K\alpha$ 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. Infrared measurements in the lattice vibration region ($400\text{--}1800\text{ cm}^{-1}$) were performed on a JASCO 5300 FT-IR spectrometer using KBr 0.05% wafer technique. Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) measurements of the solids were carried out using a Shimadzu DT 50 thermal analyzer. The TGA and DSC analyses were performed under argon or nitrogen, respectively, using 20–30 mg samples and a heating rate of $10\text{ }^\circ\text{C/min}$. The studied temperature range was $20\text{--}700\text{ }^\circ\text{C}$.

2.3. Catalytic activity

2,3,5-Trimethylphenol (99%, Aldrich) oxidation with H_2O_2 (aqueous solution 30 wt%, Cicarelli) as oxidant agent was carried out in a glass flask reactor (25 cm^3) with magnetic stirring immersed in a thermostated bath, equipped with a reflux condenser. The catalytic tests were performed varying the following parameters: hydrogen peroxide/TMP molar ratios (R) from 0 to 7.5; reaction temperatures between 25 and 60 °C and catalyst mass from 0.05 to 0.2 g. Several solvents with different dielectric constants were tested for the reaction: acetonitrile (99.5%, Cicarelli), acetone (99.5%, Aldrich), ethanol (99.5%, Cicarelli), 2-propanol (99.5%, Aldrich), 2-butanol (99.5%, Merck) and methanol (99.5%, Cicarelli). Additionally, tert-butyl hydroperoxide (70 wt%, Aldrich) as oxidant agents in the reaction was evaluated.

The reaction was monitored by taking aliquots of the reaction mixture at different reaction times. Prior to analysis, the catalyst was separated by filtration. Products were analyzed quantitatively by gas chromatography (Hewlett Packard HP-5890) with a methyl silicone capillary column (30 $\text{m} \times 0.32$ mm i.d.) and a flame ionization detector (FID), and qualitatively, by mass spectrometry GC-Mass (Shimadzu QP 5050 GC-17 A), using a HP-S (25 $\text{m} \times 0.2$ mm i.d.) capillary column. The substrate conversions are reported as mol%.

3. Results and discussion

3.1. Catalyst characterization

The UV–vis spectrum of $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ water solution had an absorbance band at $\lambda_{\text{max}} = 624$ nm with $\varepsilon_{624} = 199$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ that agree with that reported in the literature [29,30] indicating the purity of the compound. It also displayed two strong bands at 202 and 261 nm assigned to the charge transfer from bridging or terminal O 2p to W 5d (W–O–W and W–O_d, respectively) and characteristic of the polioxocompounds with Keggin structure like tungstophosphoric acid [22,31].

The FT-IR spectrum of CoW_{12} (Fig. 1) displays the characteristic bands of a Keggin-type structure at 941, 873, 762, and 451 cm^{-1} assigned to the stretching vibrations W–O_d, W–O_b–W, W–O_c–W, and Co–O, respectively, which are in agreement with the results previously reported [32]. The subscripts indicate oxygen bridging W corner sharing (b) and edge, sharing (c) oxygen belonging to WO_6 octahedra, and terminal oxygen (d). Those main characteristics bands are also present in the FT-IR spectra of CoW_{12} treated

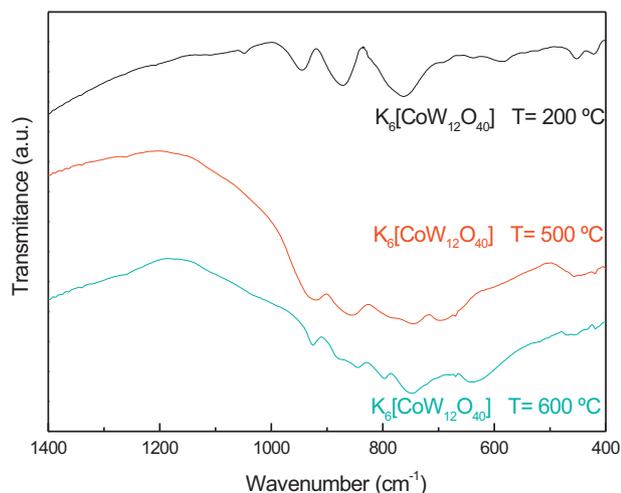


Fig. 1. FT-IR spectra of CoW_{12} samples at different temperatures.

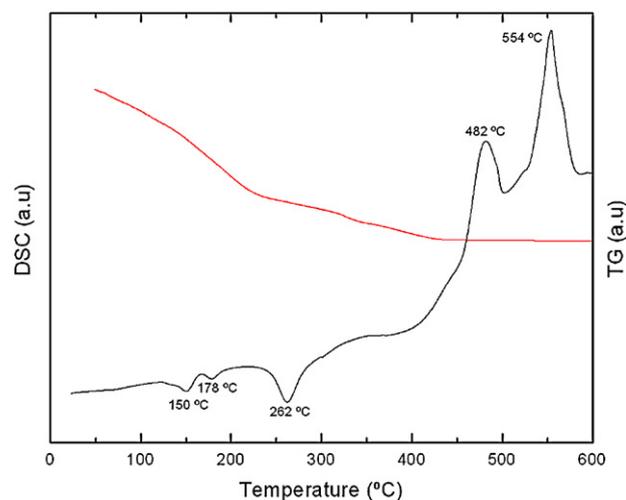


Fig. 2. Thermal analysis diagrams of CoW_{12} sample.

at 200, 300, and 400 °C. However, a new group of bands appeared in the spectrum of the heteropolycompound treated at 500 and 600 °C, as result of the transformation and decomposition of the HPC.

The DSC diagram of CoW_{12} (Fig. 2) showed three endothermic peaks at 150, 178 and 262 °C, associated with the loss of water, and two exothermic peaks at 482 and 554 °C. They are attributed to the transformation and decomposition of the $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ Keggin anion [32], that as we showed before produce changes on the FT-IR (Fig. 1). Moreover, according to the TG pattern, dehydration takes place in two main steps. The number of water molecules released per Keggin anion estimated from the weight loss ascribed to the first and second step were 11 (below 200 °C), and 6 (in the temperature range 200–450 °C), respectively, in agreement with those reported in literature [28].

The FT-IR spectrum of CoW_{12} -ZSM-5 (Fig. 3) presents the characteristics bands of $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ overlapped to those of the zeolite, suggesting that the structure of the $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ anion was preserved after the impregnation of the ZSM-5 and the thermal treatment of the final material.

The X-ray diffraction pattern of the CoW_{12} -ZSM-5 sample only displays the characteristic peaks of ZSM-5 zeolite. The absence of the lines corresponding to crystalline structures of $\text{K}_6[\text{CoW}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$ may be attributed to a high dispersion of the CoW_{12} of its presence as an amorphous phase.

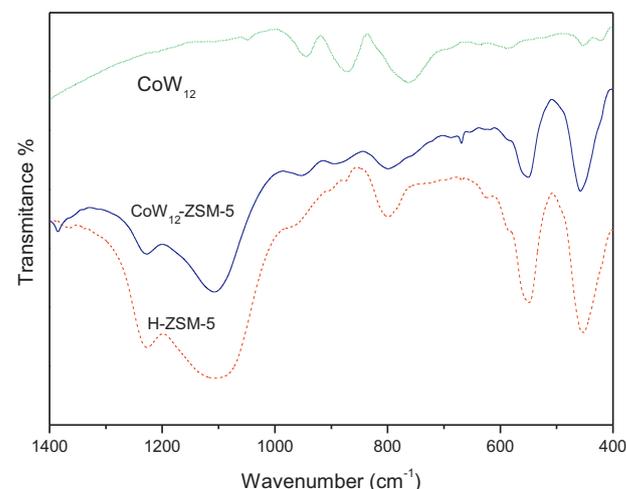


Fig. 3. FT-IR spectra of CoW_{12} , CoW_{12} -ZSM-5 and H-ZSM-5 samples.

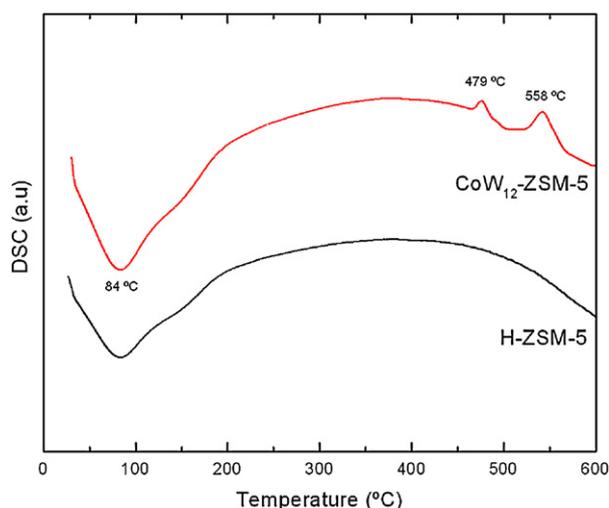


Fig. 4. DSC diagrams of supported CoW_{12} (CoW_{12} -ZSM-5) and H-ZSM-5 samples.

The DSC diagram of CoW_{12} -ZSM-5 (Fig. 4) presents an endothermic peak at 84 °C and two exothermic peaks at 479 and 558 °C. The endothermic one is also present in the ZSM-5 DSC diagram (Fig. 4) and it is assigned to the loss of water. On the other hand, the exothermic peaks are those previously assigned to the $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ anion transformation. According with these results, the thermal stability of the Keggin anion in the CoW_{12} -ZSM-5 is similar to that in the potassium salt.

3.2. Catalytic activities

3.2.1. Catalyst effect

The performance of cobalt based catalysts in the oxidation of TMP when H_2O_2 was used as oxidant and acetonitrile as solvent at 60 °C is shown in Fig. 5. It could be seen that TMP conversion continuously increases with reaction time, for CoW_{12} and CoW_{12} -ZSM-5 catalysts.

The main products of the TMP oxidation using CoW_{12} and CoW_{12} -ZSM-5 as catalysts were 2,3,5-trimethylbenzoquinone (TMBQ) and 2,3,5-trimethylhydroquinone (TMHQ), together with 2,3-dimethylmaleic anhydride and 2-hydroxyl-3,5,6-trimethyl-1,4-benzoquinone as secondary products.

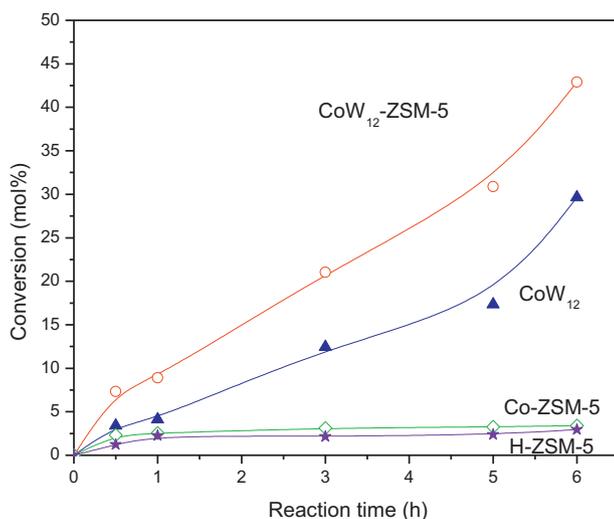


Fig. 5. Evaluation of Co-based catalysts for 2,3,5-trimethylphenol oxidation with H_2O_2 . Reaction conditions: 0.1 g of catalyst; acetonitrile as solvent; $R=5$; temperature: 60 °C.

Table 1

Comparison of catalysts for the oxidation of 2,3,5-trimethylphenol with hydrogen peroxide.

Catalyst	Conversion (mol%)	S_{TMBQ} (mol%)	S_{TMHQ} (mol%)
H-ZSM-5	2.9	86.5	–
Co-ZSM-5	3.4	68.4	1.8
CoW_{12}	29.7	38.9	21.4
CoW_{12} -ZSM-5	42.9	30.3	22.7

Reaction conditions: catalyst mass: 0.1 g; reaction temperature: 60 °C; acetonitrile as solvent; $R=5$; reaction time: 6 h.

A blank experiment was performed in identical conditions, but in absence of catalyst. In this case, the oxidation reaction occurs at a very low rate, obtaining a final conversion in the order of 1 mol% after 6 h of reaction.

According to the results presented in Fig. 5 and Table 1, CoW_{12} and CoW_{12} -ZSM-5 materials could be considered as promising catalysts due to their high activity and good selectivity to the main products (TMBQ and TMHQ).

On the other hand supported CoW_{12} (CoW_{12} -ZSM-5) seems to be considerably more active than the bulk counterpart. These results could be assigned to the presence of more dispersed $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ anions than the bulk counterpart, favoring the interaction of TMP and/or H_2O_2 with the active sites. Among that, as was reported by Kholdeeva and co-workers [9], surface hydrophilicity of ZSM-5 zeolite is a very important factor governing the catalytic activity, which ensures optimal conditions for the reagent adsorption.

Taking into account that CoW_{12} -ZSM-5 results in the most active one considering its highest conversion values (Table 1) and the good performance in terms of selectivity toward TMBQ (30 mol%) and TMHQ (23 mol%), this catalyst was chosen to study reaction parameters effects.

3.2.2. Oxidant effect

The TMP oxidation reaction was extremely sensitive to the nature of the oxidant used. The results obtained for TMP oxidation using CoW_{12} -ZSM-5 with H_2O_2 (30 wt%) and TBHP (70 wt%) are shown in Table 2.

Using TBHP the reaction was highly selective toward the formation of TMBQ, while no TMHQ was obtained using this oxidant. Since TMP conversion was considerably higher with H_2O_2 than TBHP, the following studies were done with this oxidant.

3.2.3. Influence of solvent

It is well-known that the solvent plays an important and sometimes decisive role in the catalytic behavior of a catalyst [25,33]. Therefore, the effect of solvents on the activity of CoW_{12} -ZSM-5 for TMP oxidation was studied in the current catalytic system at 60 °C, H_2O_2 as oxidant agent with an oxidant/substrate molar ratio of 5 and 0.1 g of the catalyst. Table 3 shows the influence of solvents such as acetonitrile, acetone, methanol, ethanol, 2-propanol and 2-butanol on TMP conversion after 7 h of reaction. These solvents were chosen because they form a single phase with the organic substrate and the aqueous hydrogen peroxide solution, so mass transfer problems associated to the presence of different liquid

Table 2

Effect of the oxidant in TMP oxidation.

Oxidant	Conversion (mol%)	S_{TMBQ} (mol%)	S_{TMHQ} (mol%)
H_2O_2	42.9	30.3	22.7
TBHP	10.2	56.6	–

Reaction conditions: 0.1 g CoW_{12} -ZSM-5; 60 °C; acetonitrile as solvent; 4 ml of oxidant; reaction time: 6 h.

Table 3
Oxidation of TMP with H₂O₂: influence of different solvents on conversion.

Solvents	Dielectric constant	Conversion (mol%)
Acetonitrile ^a	37.5	42.9
Acetone ^a	20.7	31.5
Methanol ^b	32.7	82.5
Ethanol ^b	24.5	37.9
2-Propanol ^b	19.9	31.4
2-Butanol ^b	16.5	29.7

Reaction conditions: 0.1 g CoW₁₂-ZSM-5; 60 °C; R = 5; reaction time: 7 h.

^a Aprotic.

^b Protic.

phases were avoided. It can be seen that the activity increases with solvent polarity for both the protic and aprotic series.

Another important information obtained from this study involves the reaction mechanism, since TMP conversion was noticeable lower when isopropyl alcohol was used as solvent (Fig. 6) and it is well known that these alcohol act as radical scavenger. So, an homolytic mechanism previously proposed by Kholdeeva et al. [13] which includes the formation of the ArO• phenoxyl radical that with further transformations results in the TMBQ should be present in this reaction system. Since no coupling dimers (biphenol, polyphenylene oxide) were detected, we assume that this reaction is favored with respect to the other secondary radical reactions proposed by the authors.

As TMHQ is obtained as one of the main products, we propose for our reaction system a combined mechanism which includes a heterolytic pathway of electrophilic hydroxylation via the formation of the TMHQ [34,35].

It was found that in the evaluated reaction conditions, TMP oxidation showed the highest conversion when the reaction was performed in methanol media, which could be attribute to the polarity and proticity of the solvent which can make different phases uniform, thereby favoring mass transfer.

According to Sheldon et al. [36] and other recognized researchers in the heterogeneous catalysis field, lixiviation problems could not be ruled out by experiments demonstrating that the catalysts can be recovered and recycled without apparent loss of metal content or activity. So, as was proposed by them, we proceed to filtrate the catalyst from the reaction system after three hours and leave the filtrate at the same reaction conditions.

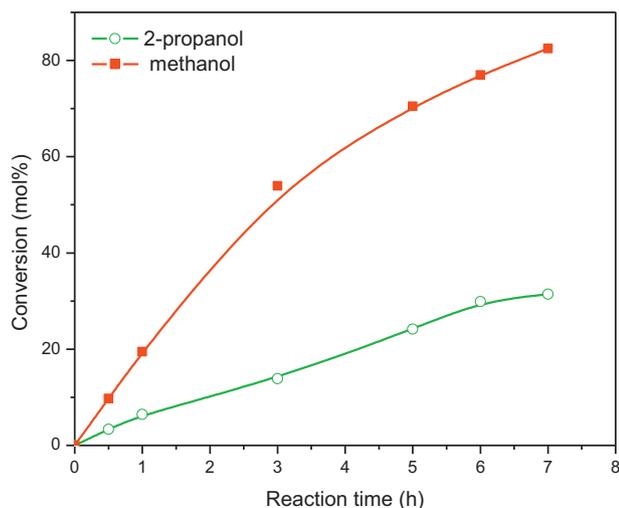


Fig. 6. Effect of a radical scavenger in TMP oxidation. Reaction conditions: 0.1 g CoW₁₂-ZSM-5; 60 °C; R = 5.

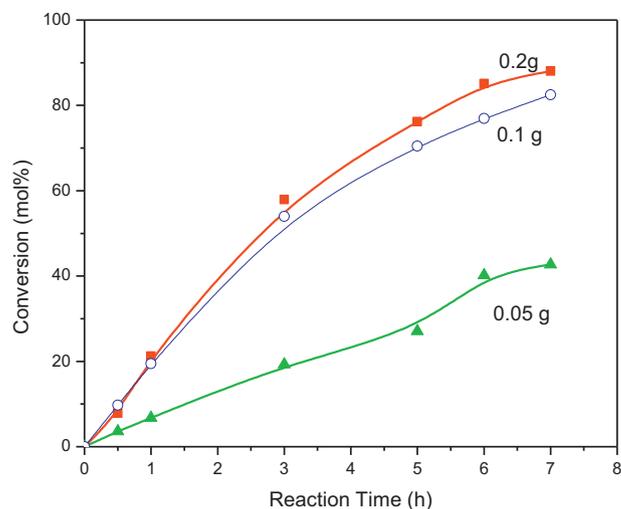


Fig. 7. Effect of CoW₁₂-ZSM-5 amount in TMP conversion. Reaction conditions: methanol as solvent; R = 5; temperature: 60 °C.

In this situation we observed that TMP conversion was not completely stopped after the catalyst separation. This result is a hint that leaching of active species could take place.

However, as we have observed that the reaction proceeds not only by a heterolytic pathway, but also by a combined mechanism, it is possible that the radicals formed during the first reaction hours, continue the oxidation process even in the absence of the catalyst.

3.2.4. Catalyst mass

Fig. 7 displays the effect of CoW₁₂-ZSM-5 amount in the reaction system, keeping constant TMP and H₂O₂ initial concentrations in methanol media. A noticeable increment in TMP conversion (from 42.9 to 82.5 mol%) is observed when catalyst mass goes from 0.05 g to 0.1 g. However, a further increment from 0.1 g to 0.2 g does not induce such important increment (from 82.5 to 88.1 mol%). For this reason, 0.1 g was adopted as the optimum catalyst amount to produce TMBQ.

3.2.5. Oxidant concentration

Hydrogen peroxide concentration in the reaction system has a considerable effect on the oxidation of TMP as has been demonstrated considering four different oxidant to TMP molar ratios at fixed amount of TMP (1 g), catalyst (0.1 g), solvent (methanol, 10 ml) and temperature (60 °C). As it is shown in Fig. 8, TMP conversion improved from 16 to 83 mol% as result of the increment of the H₂O₂ to TMP molar ratio from 2.5 to 5. The results also suggest that a large amount of oxidant is not an essential condition in improving the catalytic performance of the catalyst, since TMP conversion decays when oxidant/substrate molar ratio goes from 5 to 7.5. The reason for this decreasing trend may be due to dilution of the reaction mixture by the presence of larger amount of water molecules in H₂O₂ solution [37].

When H₂O₂ concentration was lower, TMBQ production was negligible obtaining only TMHQ as main product. This result could be explained by the heterolytic pathway [35] that involves a multi-step oxidation from 2,3,5-trimethylphenol to 2,3,5-trimethylhydroquinone and then to 2,3,5-trimethylbenzoquinone. So, when hydrogen peroxide has low concentration in the system, the last step is avoided.

On the other hand, some unproductive decomposition of the oxidant in the presence of the CoW₁₂-ZSM-5 catalyst could be observed since TMP conversion was not complete in any case.

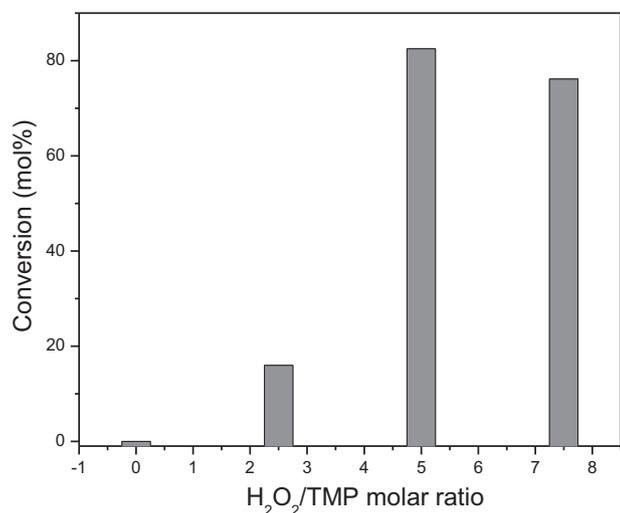


Fig. 8. TMP oxidation over CoW₁₂-ZSM-5 catalyst. Reaction conditions: catalyst mass: 0.1 g; reaction temperature: 60 °C; reaction time: 7 h; solvent: methanol.

3.2.6. Effect of reaction temperature

TMP oxidation over CoW₁₂-ZSM-5 was found to be influenced by reaction temperature as could be observed from Fig. 9 when other reaction conditions were kept constant. TMP oxidation was found to improve with increasing the reaction temperature from room temperature to 60 °C, especially in the range from 50 to 60 °C obtaining a 40 mol% of enhancement in TMP final conversion value. Temperatures above 60 °C were not evaluated since methanol boiling point is 64.7 °C.

TMBQ and TMHQ selectivities were not considerably affected with reaction temperature variations. So, a temperature increment favors both: TMP conversion and TMBQ and TMHQ yields.

Effective activation energy (E_a) was estimated from the plot of $\ln k$ vs $1/T$ presented in Fig. 10. According to this results E_a was 94.19 kJ/mol, this shows that the reaction rate is not limited by the diffusion of the reactants to the active catalytic sites, because E_a for diffusion-limited process is expected to be considerably lower [38].

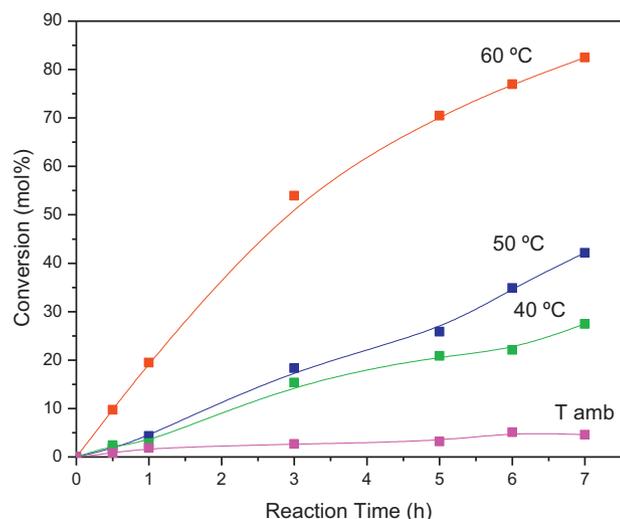


Fig. 9. Reaction temperature effect on TMP oxidation with hydrogen peroxide. Reaction conditions: 0.1 g of CoW₁₂-ZSM-5; methanol as solvent; $R=5$.

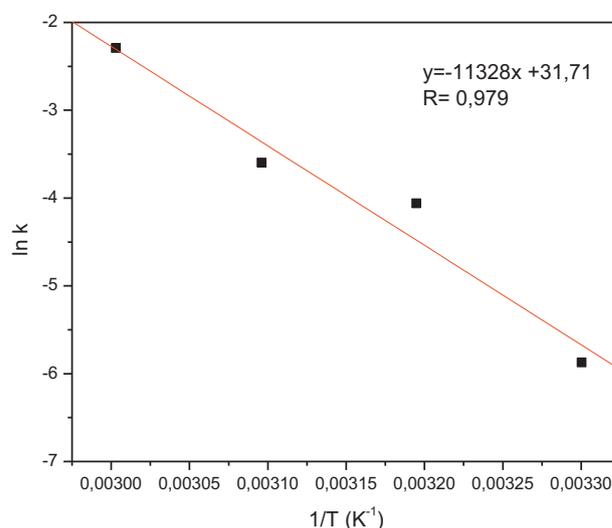


Fig. 10. $\ln k$ vs $1/T$ plot for the TMP oxidation with H₂O₂ over CoW₁₂-ZSM-5. Reaction conditions: 0.1 g of CoW₁₂-ZSM-5; methanol as solvent; $R=5$.

4. Conclusions

CoW₁₂ supported on ZSM-5 zeolites were successfully synthesized employing the wet impregnation method to deposit the heteropolyanion over the zeolite matrix. The materials so far prepared were characterized by different techniques to confirm the species and structures present. The activity of CoW₁₂-ZSM-5 was evaluated by studying the oxidation of 2,3,5-trimethylphenol in the presence of hydrogen peroxide as oxidant.

The effect of various experimental conditions was also studied. Best results were obtained employing H₂O₂ as oxidant, 0.1 g of catalyst mass, a reaction temperature of 60 °C and methanol as solvent. A combined homolytic and heterolytic mechanism is proposed. Finally, an effective E_a of 94.19 kJ/mol was also calculated for this reaction system, indicating no diffusional limitations.

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