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A greener method to obtain a key intermediate of Vitamin E over Cu-ZSM-5

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Abstract

The catalytic oxidation of 2,3,5-trimethylphenol was performed over transition metals modified ZSM-5 zeolites employing hydrogen peroxide as oxidant under mild reaction conditions. Catalysts samples were characterized by several techniques (XRD, FTIR, BET, AA) and cristallinity and orthorhombic symmetry were confirmed for all of them. Best catalytic results were obtained for Cu-ZSM-5 sample, so further activity studies were done over this material. 2,3,5-trimethyl-1,4-benzoquinone was obtained as the main product of the selective oxidation. 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. According to the obtained results, an apparent activation energy of 52.33 kJ/mol was calculated.

Keywords: 2,3,5-trimethylphenol; 2,3,5-trimethyl-1,4-benzoquinone; hydrogen peroxide; Cu-ZSM-5; reaction parameters.

Introduction

Catalytic reactions, one of the key issues in the fine chemicals industry, seek to reduce wastes and bring economic benefits. Heterogeneous catalysis is generally viewed as an effective method for oxidation reactions. Due to environmental considerations and safety concerns, there is a growing tendency to replace homogeneous methods which generate copious wastes by heterogeneous ones. One of its great advantages is the easy catalyst recovery without tedious experimental workup and higher selectivities to the desired products. These advantages together with the absence of wash water containing the dead catalyst may lower the production costs[1,2]. As a result, supported metal catalysts play a key role in many industrially important chemical processes. In this paper, the application of catalytic oxidation in the synthesis of vitamin E intermediate is reported.

Due to its antioxidant properties and biological activity, vitamin E is of economic and industrial interest. The term ''vitamin E'' refers to a group of four tocopherols and four tocotrienols with a chroman core. Tocopherols have attracted more attention than tocotrienols because of their superior biological relevance[3].

Adequately substituted benzoquinone derivatives, in particular 2,3,5-trimethyl substituted ones, are key intermediates in the early stages of the industrial synthesis of α-tocopherol, which is the most active component of the group of tocopherols that compose vitamin E. Hence, the design of selective catalytic methods for α-tocopherol production on a large scale is particularly appealing from an industrial viewpoint[4,5]. These industrial requirements have led to increased efforts for catalyst design and preparation[6].

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The use of hydrogen peroxide as oxidizing agent in the presence of catalysts has become a clean and effective alternative among other catalytic oxidation processes and is commonly named as CWPO (catalytic wet peroxide oxidation)[7,8]. Hydrogen peroxide does not produce any harmful by-products, since it just produces water. Is a nontoxic reactant, improves oxidation efficiency and requires milder reaction conditions. When employing homogeneous catalysts, there are two major drawbacks, namely a narrow acidic pH range and the need for removing the catalyst. The use of heterogeneous materials as catalysts based on low-valence transition metals appears as a promising option to solve these problems, since oxidation efficiencies are relatively high and pH sensitivity is lower compared with homogeneous catalysts at the same operating conditions[9].

Therefore, a variety of catalysts containing iron, copper and other transition metal precursors supported on different materials (oxides, clays, zeolites, natural and synthetic polymers) have been probed in CWPO reactions[10,11]. The zeolites may offer interesting opportunities as catalysts supports, since they combine three important characteristics: large pores, high Si/Al synthesis ratio, and a tridirectional network of pores. The ZSM-5 zeolites (MFI structure) formed by a three-dimensional medium pore system (openings of 5–5.5 Å) are interesting to apply in this oxidation process [12,13].

Copper is a common metal used in oxidation catalysis studies. As other low valence transition metal ions, Cu^{2+} activates hydrogen peroxide, so many investigations have been done in this field[14,15]. There are various reports on copper-containing porous and nonporous heterogeneous catalysts, which were reported to be active in the selective oxidation of a variety of organic compounds in the presence of atom-efficient oxidants by the well-known Fenton-type mechanism[16-18].

This work was undertaken to study the catalytic oxidation of 2,3,5-trimethylphenol (TMP) to 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) with H_2O_2 using transition metal modified zeolite catalysts. In one of our previous papers, the use of supported $K_6[CoW_{12}O_{40}] \cdot 6H_2O$ with Keggin structure over ZSM-5 zeolites as active and selective solid catalysts for the oxidation of TMP, employing aqueous hydrogen peroxide as oxidant, was reported [19]. However, higher yields to TMBQ were obtained using Cu-ZSM-5. The use of metal-modified zeolites gave interesting results considering the easiest method to obtain these materials.

2. Experimental

2.1 Catalysts preparation

The standard literature procedure [20] was employed to synthesized ZSM-5 zeolite with a Si/Al molar ratio of 17. The hydrothermal crystallization was done in the Na_2O-Al_2O_3-SiO_2 system, using TPAOH (Tetrapropylammonium Hydroxide) as a structure directing agent. The obtained gel reached a pH > 9 and was maintained on a Teflon autoclave at 120-160 °C for 10-12 days under self-generated pressure. Subsequently, after the extraction of the reaction product of the reactor, it was washed with distilled water and dried at 110 °C for 12 h. The structure directing agent (TPA) was desorbed in N_2 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.

To obtain the NH_4^+-form of the catalyst, the Na-zeolite was ion-exchanged with NH_4Cl (1 M) solution for 40 h at 80ºC. Further thermal treatments were applied to it in order to obtain the protonic form of the zeolite (H-ZSM-5): desorption for 12 h in N_2 flow (10 ml/min) at 500ºC and finally calcined in air at 500ºC for 8 h.

Transition metals were incorporated in the zeolite matrix by the wetness

impregnation method. For this purpose, the ammonium form of the zeolite was

suspended in an aqueous solution of the proper salt: $FeCl_2.4H_2O$ (Mallinckrodt), for Fe-

ZSM-5; $Cu(C_2H_3O_2)_2.H_2O$ (Mallinckrodt), for Cu-ZSM-5 and $CrCl_3.6H_2O$ (Fluka), for

Cr-ZSM-5. The water was evaporated using a rotator–evaporator at 80°C under vacuum

until complete dryness. Then samples were dried at 110 °C and desorbed in N_2 flow at

500 ºC for 12 h, followed by calcination in air at 500 ºC for 8 h to obtain M-ZSM-5

samples.

2.2 Catalysts characterization

The content of metal in each sample 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.

Structure and cristallinity of the samples were studied by X-ray diffraction

patterns collected in air at room temperature in a Philips diffractometer using CuKα

radiation. Diffraction data were recorded between 2θ= 5º and 60º at an interval of 0.05º.

A scanning speed of 2º/min was used.

BET surface area determinations were carried out with an ASAP 2000

equipment.

The infrared spectra of H-zeolites and M-zeolites were recorded on a JASCO

5300 FTIR spectrometer. The samples were pressed into self-supporting wafers (8-10

mg/cm^2). Spectral scanning was done from 4600 to 400 cm^{-1} in 16 consecutive registers

of 4 cm^{-1} resolution each one. In order to evaluate the interaction of pyridine over

Lewis and Brönsted acidic sites, pyridine (3 Torr) was adsorbed at room temperature for

12 h and desorbed for an hour at different temperatures at 10^{-4} Torr. The experiments

were carried out using a thermostatized cell with CaF_2 windows connected to a vacuum

line. The numbers of Brönsted and Lewis acid sites were quantified using the literature

data of the integrated molar extinction coefficients [21], resulting in no dependence of the

integrated coefficients on the catalysts or strength of the sites. The FTIR spectra in the

lattice vibration region (400-1400 cm^{-1}) were performed using KBr 0.05% wafer

technique.

2.3 Catalytic activity

To study the oxidation of 2,3,5-trimethylphenol (99 %, Aldrich) a glass flask

reactor (25 cm^3) equipped with a reflux condenser was immersed in a thermostatized

bath and the reaction was carried out by adding H_2O_2 aqueous solution (30 wt%,

Cicarelli), confirmed by permanganometric titration. The system was constantly

magnetic stirred at 1500 rpm to avoid external mass transfer resistance. The catalytic

tests were performed at 60°C using 0.1 g of the catalyst and different molar ratios of

TMP/hydrogen peroxide. 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) and 2-butanol

(99.5%, Merck). The reaction was monitored by taking aliquots of the reaction mixture

at different reaction times. Prior to analysis, the catalyst was separated from the solution

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

The main characterization results of the samples under study are resumed in

Table 1. For each catalyst, metal loading, total surface area and percentage of

crystallinity are listed.

Table 1. Physicochemical characterization of the samples.

Catalyst	Metal Loading (%wt)	Surface area (m^2/g)	Crystallinity (%)	
	AA	BET	XRD	FTIR[a]
H-ZSM-5	---	358	100	>99
Cu-ZSM-5	3.0	337	>98	>99
Cr-ZSM-5	2.7	350	>98	>97
Fe-ZSM-5	2.9	345	>98.5	>99

[a] FTIR in the fingerprint zone of the materials (400-1400 cm^{-1}).

Table 1 illustrates that the rigorous experimental conditions employed during

chemical and thermal treatments did not affect the structural characteristic and

orthorhombic symmetry of the catalysts. The signals characteristic of the matrix ZSM-5

are observed at: $2\theta = 23$-24 and $2\theta = 7$-9 degrees, appearing unalterable after the

incorporation of the different metal cations.

Pyridine adsorption over acid materials is a common technique to characterize

the acid sites nature and strength by FTIR spectroscopy based on the observation of the

vibrational perturbation that is undergone when this kind of probe-molecules adsorb on

them [22]. Acid strength of the sites is determined according to the ability to retain

pyridine as temperature is increased. Pyridine was adsorbed at room temperature over

the samples and desorbed at different temperatures under vacuum for an hour.

IR spectra of pyridine adsorbed on H-ZSM-5 and M-ZSM-5 samples are shown

in Figure 1. Bands at 1452-1456 cm^{-1} (υ 19B mode) and 1612 cm^{-1} (υ 8A mode),

corresponding to Py interaction with Lewis acid sites (L-Py) could be observed, as well

as bands at 1547 cm^{-1}(υ 19B mode) and a shoulder at 1635 cm^{-1} (υ 8A mode), indicative

of the interaction with Brönsted acid sites (PyH$^+$) [23] . The band at 1490-1495 cm^{-1}

corresponds to the vibration of adsorbed Pyridine over both Brönsted and Lewis acid

sites [24]. Bands corresponding to hydrogen-bonded pyridine (1440-1447 cm^{-1} and 1580-

1600 cm^{-1}) and physically adsorbed pyridine (1439 and 1580 cm^{-1}) [25] are not

considered since the spectra shown were taken after desorbed at 350 ºC.

H-ZSM-5 spectrum presents an important signal of Brönsted sites and some L-

Py resulting from Al^{3+}. Upon introduction of metal cations in the pentasil matrix, new

EDA adduct of pyridine-Lewis acid sites at 1454 cm^{-1} (O-M) were generated, stronger

than the well-known Lewis aluminum acid sites of the zeolite framework (1456 cm^{-1}),

since they retain more pyridine than the parent H-ZSM-5 material after outgassing at

350ºC. The number of Brönsted acid sites (1545-1550 cm^{-1}) decreases as the number of

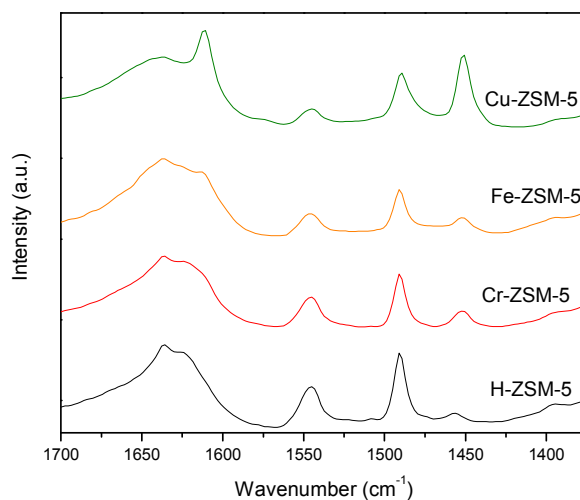Lewis acid sites (1450-1460 cm^{-1}) increases for M-ZSM-5 samples.

Figure 1. FTIR spectra of pyridine adsorbed at room temperature and desorbed at 350 ºC and 10^{-4} Torr.

3.2. Catalytic activity of M-ZSM-5 in TMP selective oxidation

The catalytic results for the selective oxidation of TMP obtained after 6 h of reaction over a series of transition metal modified ZSM-5 zeolites are presented in Table 2 employing 0.1g of each catalyst, acetonitrile as solvent and a molar ratio of 0.2 of substrate/hydrogen peroxide. The reaction catalyzed by H-ZSM-5 without metal loading only gives a 2.95 mol% of TMP conversion. Previously, we had evaluated Co-ZSM-5 as catalyst for TMP oxidation, but as just a 3.4 mol% was obtained after 6h, it could not be consider as suitable for this reaction[19]. Even when all the M-ZSM-5 samples evaluated had a similar Metal wt%, Copper one (Cu-ZSM-5) is considerable more active than the other counterparts with ca. 80 mol% of TMP conversion. According with these results and analyzing FTIR ones (Figure 1 and Table 2), it is possible to suppose that Lewis acid sites favors TMP conversion, probably by a selective interaction between substrate molecules and Lewis acid sites. Similar results

were obtained by our group when studying styrene oxidation over Cobalt modified

zeolites [26].

The main product of the TMP oxidation using M-ZSM-5 as catalysts was 2,3,5-

trimethyl-1,4-benzoquinone (TMBQ), together with 2,3,5-trimethylhydroquinone

(TMHQ), 2,3-dimethylmaleic anhydride and 2-hydroxyl-3,5,6-trimethyl-1,4-

benzoquinone as secondary products.

Table 2. M-ZSM-5 as catalysts for TMP oxidation

Catalyst	Conversion (mol%)	Selectivity$_{TMBQ}$ (mol%)	Acid Sites (mmol Py/mg)	
			Lewis	Brönsted
H-ZSM-5	2.95	86.4	0.0037	0.0268
Cu-ZSM-5	77.6	85.5	0.0104	0.0138
Cr-ZSM-5	15.96	92.3	0.0091	0.0219
Fe-ZSM-5	9.68	82.1	0.0061	0.0145

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.

Considering that Cu-ZSM-5 showed the best catalytic behavior for the synthesis

of TMBQ of all the materials evaluated, this sample was chosen to evaluate the

influence of the different reaction parameters.

3.2.1. Influence of solvent properties on TMP oxidation

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 [27]. A series of both

protic (methanol, 2-propanol, 2-butanol) and aprotic (acetonitrile, acetone) solvents were

tested for this oxidation. When studying the influence of the proticity of the solvent on

TMP oxidation over Cu-ZSM-5 samples, we found that aprotic solvents give better

results. As could be seen from Figure 2 and Table 3, TMP conversion values are larger

for aprotic solvents and increases with Dielectric Constant values. According with

Corma et al. [28], the enhancement on TMP conversion as the polarity of the aprotic

solvents increases, could be explained by the increase of substrate concentration in the

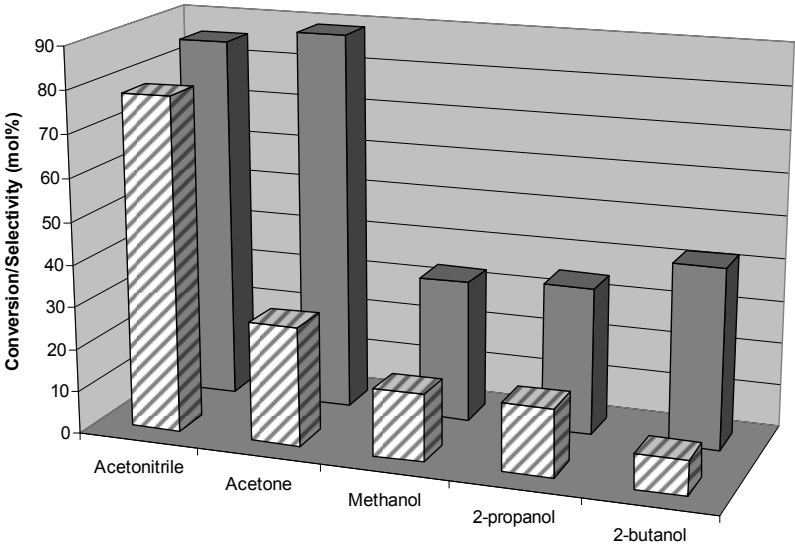hydrophilic pores of the zeolite as Dielectric Constant values growth.

Figure 2. Effect of solvent on Cu-ZSM-5 activity and selectivity to TMBQ. Symbols:

(▨) conversion and (▦) selectivity

Table 3. Solvents properties

Solvents	Dielectric Constant	Boiling point (ºC)
Acetonitrile[a]	37.5	81.6
Acetone[a]	20.7	56.3
Methanol[p]	33	65
2-propanol[p]	18	82
2-butanol[p]	16.5	99.5

a: aprotic; p: protic

In the case of protic solvents a competition between TMP and alcohol solvent molecules take place at the hydrophilic surface of the catalyst. That is why catalyst activity decreases for all the protic solvents evaluated.

When considering TMBQ selectivity, it could be seen from Figure 2 that aprotic solvents give better results. Conversely, in the case of protic solvents, lower selectivities to the desired product are obtained and C-C and C-O coupling products are present as minor products but indicating the occurrence of one electron oxidation mechanism that involves the formation of phenoxyl radicals, as found by Kholdeeva et al. [29].

To reach better TMBQ yields, acetonitrile was chosen as the optimal solvent for TMP oxidation over Cu-ZSM-5.

3.2.2. Catalyst loading effect

The effect of catalyst concentration in TMP oxidation was evaluated using different loadings of Cu-ZSM-5 and keeping constant substrate and oxidant concentrations (Figure 3). Catalyst mass was varied from 0 – 0.2 g and TMP conversion

joined this increase trend until 0.1 g, then a soft decay could be observed. This tendency

may be related to an auto decomposition of hydrogen peroxide that gives water and

oxygen as products ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) [30].

It should be noted that TMBQ selectivity remain constant at every catalyst

concentration evaluated, indicating that the reaction mechanism is the same in all the

situations. Because of the simultaneously occurring of H_2O_2 decomposition and TMP

oxidation reactions, the catalyst loading has an optimal value for obtaining the highest

TMP conversion. So, since TMP conversion was considerably higher with 0.1 g of Cu-

ZSM-5, our attempts to optimize reaction conditions were done employing this catalyst
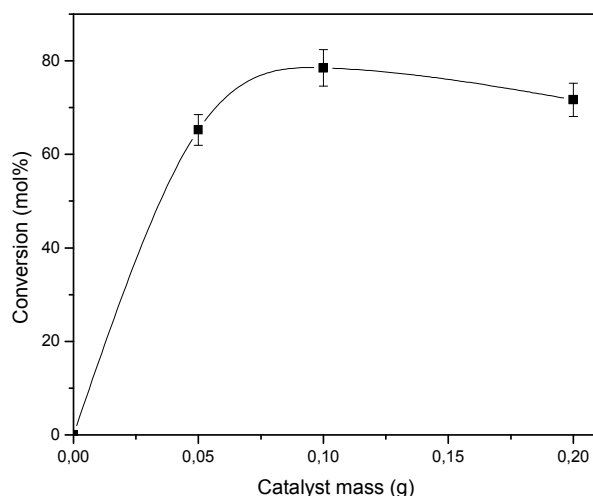
mass.

Figure 3. Catalyst mass influence on TMP conversion

Catalytic activity dependence on copper content was evaluated in the same

conditions than catalyst mass evaluation but employing 0.1g of each material to ensure

optimal conditions. TMP conversion results are shown in Figure 4. Catalytic activity

increases as copper content up to 3 wt%, but then remains quiet constant with a slight

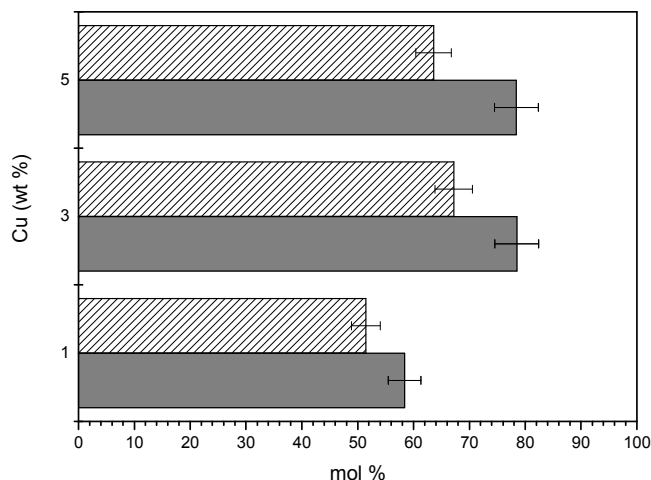reduction on TMBQ yield at higher copper content.

Figure 4. Dependence of TMP conversion (■) and TMBQ (▨) yield over Cu-ZSM-5 catalyst on Cu loading. Reaction conditions: Acetonitrile, as solvent, 60 ºC, R=0.19.

3.2.3. Catalyst recycling

In order to evaluate catalyst stability, Cu-ZSM-5 was easily recovered by filtration, washed, dried, calcined and reused. The calcination step at 500 ºC was necessary in order to remove the organic products that could be adsorbed on catalyst surface and blocking the active sites of the catalyst. Results of TMP conversion and TMBQ yield after 5 h of reaction are shown in Figure 5.

No remarkable changes in conversion or TMBQ yield were observed after the second cycle of the reused catalyst as an evidence of no leaching of the active species. It is possible to consider Cu-ZSM-5 as reusable catalysts since the 80% of the initial catalytic activity was preserved after five consecutive reuses.

When metal content in the sample was determined after the fifth cycle, a considerable reduction of 1.1 Cu wt% was obtained. It is possible to induce that metal leaching takes place after the second use and then remains constant since catalyst activity did not present significant variations.
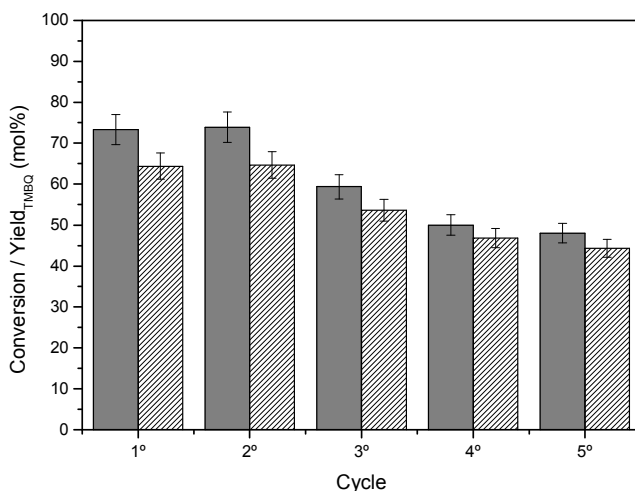
Figure 5. Stability of Cu-ZSM-5 after five cycles. TMP conversion (■) and TMBQ (▨)

yield. Reaction conditions: Acetonitrile, as solvent, 60 ºC, R=0.19.

3.2.4. Effect of H_2O_2 concentration

Although aqueous H_2O_2 is generally regarded as an environmentally friendly

"green" reagent because it gives water as the sole by-product of oxidation [31], the amount

of hydrogen peroxide will affect the conversion of TMP and the selectivity to TMBQ.

So, the effect of H_2O_2 concentration was studied at 60 ºC by varying the molar ratio of

hydrogen peroxide at constant concentrations of substrate and catalyst in the reaction

mixture. It should be pointed out that in the runs done in absence of catalyst or without

oxidant, no TMP conversion was observed, demonstrating that the activation of

hydrogen peroxide by the catalyst is necessary [32].

When considering oxidant concentration effect, it could be seen that two zones

exists in the graph of the evolution of TMP conversion (Figure 6). Initially, conversion

values goes from 11 to 79 mol% when varying hydrogen peroxide initial concentration

from 0.68 to 2.71 mol/L, but then, on a further increment of the peroxide concentration

to 5.43 mol/L, just a 10 mol% in conversion enhancement was obtained.

It is also possible to observe a decreasing trend on TMBQ selectivity with

oxidant enhancement, probably due to a further oxidation of the quinone to 2,3-

dimethylmaleic anhydride, even when it continues being the main product. So,

according with these results, to reach the maximum TMBQ yield, 2.71 mol/L of

hydrogen peroxide should be employed. When employing this initial concentration of

the oxidant, a 17% of efficiency of H_2O_2 for TMP oxidation was obtained. Hydrogen

peroxide efficiency was calculated by the following equation:

$$Eff_{H2O2} = \frac{TMBQ\,obtained\,(moles)}{H_2O_2\,consumed\,(moles)} \times 100$$

This value is in accordance with those published by Wang et al. in styrene

oxidation with hydrogen peroxide[33]. For lower concentrations (0.68 mol/L), oxidant

efficiency was slightly higher (20%) and for the highest hydrogen peroxide

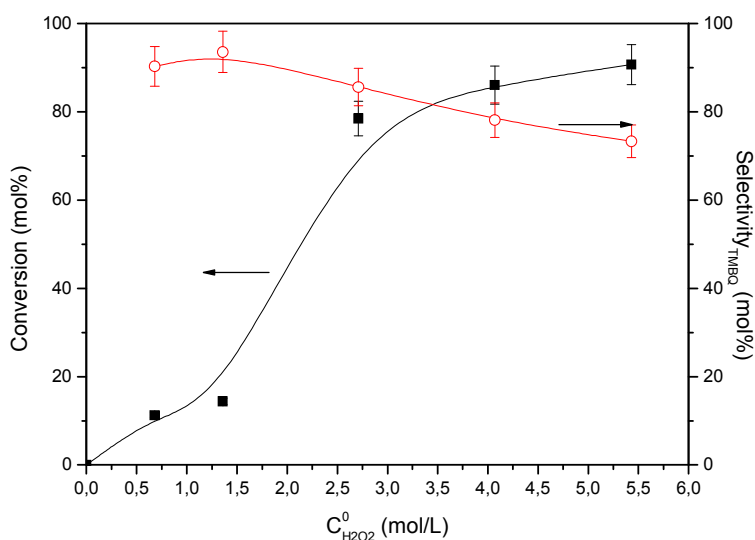concentration evaluated (5.43 mol/L), the efficiency was just 12%.

Figure 6. Effect of H_2O_2 concentration on TMP conversion (■) and TMBQ selectivity (○).

To avoid the unproductive decomposition of the oxidant in the presence of the Cu-ZSM-5 catalyst, oxidant was added in two steps: at the beginning of the reaction and after three hours, but conversion values did not suffer considerable change.

In order to get a better knowledge of the reaction mechanism, a radical scavenger (isopropyl alcohol) was added after 30 minutes of reaction (Figure 7). When the radical scavenger was added, TMP conversion suffers an important reduction of ~ 30 mol%. As we proposed in our previous paper on TMP oxidation employing supported heteropolycompounds as catalysts [19], an homolytic mechanism previously informed by Kholdeeva et al. [34], which includes the formation of the ArO· phenoxyl radical that with further transformations results in the TMBQ, should be present in this reaction system. It is well-known that Cu^{2+} activates hydrogen peroxide generating hydroxyl radicals in the Fenton-like reaction, so it is possible to assume the presence of a radical mechanism 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 group of Kholdeeva.

As TMHQ is obtained as the main secondary product, we propose for our reaction system a combined mechanism which includes a heterolytic pathway of electrophilic hydroxylation via the formation of the TMHQ [35, 36].
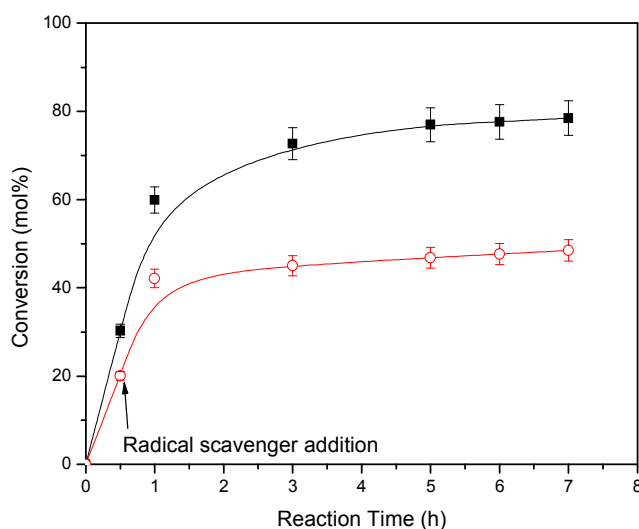
Figure 7. Effect of the introduction of a radical scavenger on TMP conversion: (■) without radical scavenger reaction; (○) adding isopropyl alcohol after 30 min. Reaction conditions: 0.1 g of Cu-ZSM-5; acetonitrile as solvent; Temperature: 60 ºC.

3.2.5. Influence of the initial concentration of TMP

To study the effect of substrate initial concentration, a series of reactions varying this parameter were done maintaining constant hydrogen peroxide and catalyst concentrations. All the experiments were done at 60 ºC employing acetonitrile as solvent and the results are presented in Figure 8. As could be observed from the figure, TMP conversion increases with reaction time and reach a constant value after 4 h of reaction at every substrate initial concentration. When substrate concentration was varied from 1.5 mmol to 11 mmol, conversion values suffered a 47 mol% of decay indicating that the decrease in oxidant and catalyst to substrate ratio is not enough to provide a successful contact between the acting parts. With the obtained results it was also possible to determine a second order with respect to TMP as could be seen in the inset of Figure 8.
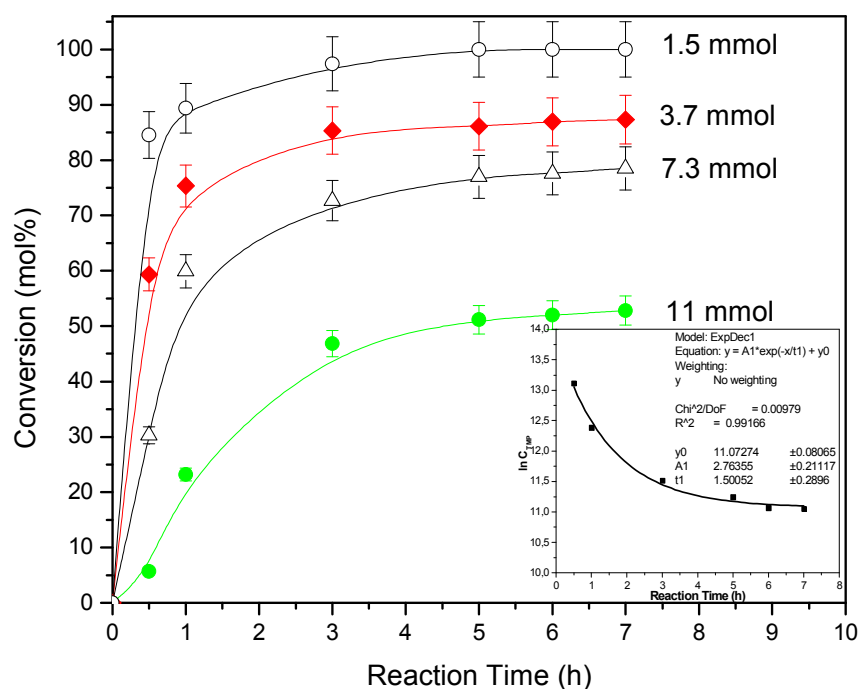
Figure 8. The reaction profile for TMP oxidation varying substrate initial concentration.

Inset: Determination of reaction order.

3.2.6. Evaluation of reaction temperature

The effect of reaction temperature on catalytic activity of Cu-ZSM-5 for TMP

selective oxidation was investigated by varying this parameter from 25 to 70 °C (Figure

9). TMP, hydrogen peroxide and catalyst concentrations were kept constant and

acetonitrile was used as solvent. The catalytic results after 7 h of reaction suggest that

there is an optimum reaction temperature. Conversion of TMP increases when reaction

temperature goes from room temperature (25°C) to 60°C, but when a higher value (70

°C) was tested a decay in TMP conversion was obtained.

It is worth noting here that when temperature was higher than 60 °C, TMBQ

selectivity was not affected, but the yield of the desired product was less than that

previously obtained. This result could be related with hydrogen peroxide thermal

decomposition over Copper zeolite when reaction temperature is higher than 60 ºC
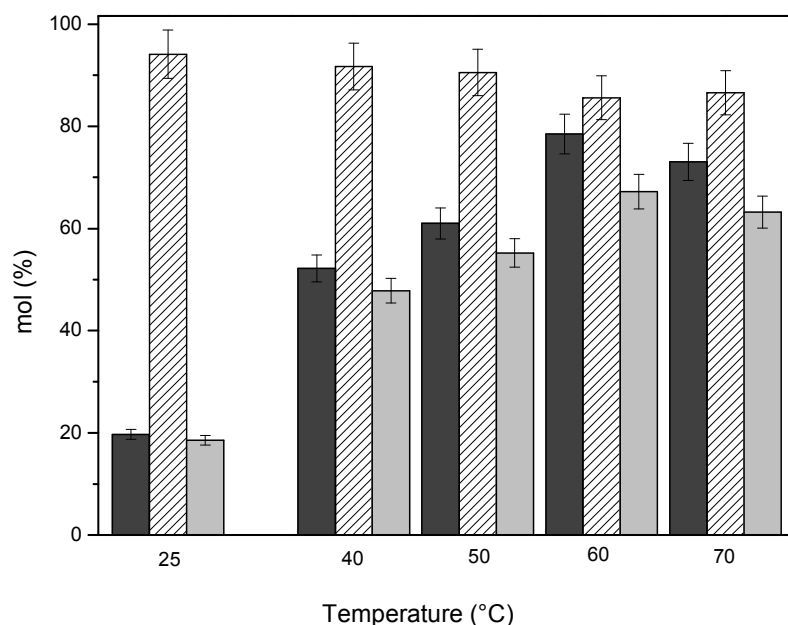
producing a lesser substrate conversion.

Figure 9. Effect of reaction temperature on TMP conversion, TMBQ selectivity and

yield over Cu-ZSM-5. Symbols:(■) conversion, (▨) TMBQ selectivity and (■) yield.

The effective activation energy (Ea) estimated from the lnR0 – 1/T plot (Figure

10) was 52.33 KJ/mol. This shows that the reaction rate is not limited by the diffusion

of reactants to the active catalytic sites, because Ea for diffusion-limited process is

expected to be considerably lower. This activation energy is very close to that reported

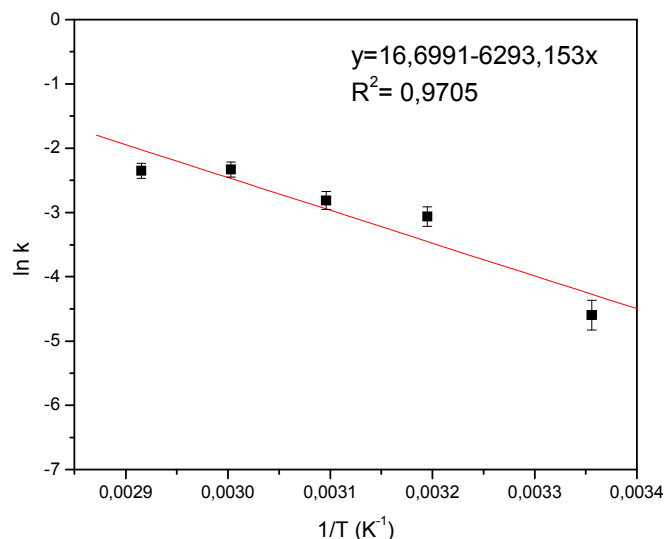by Trukhan et al.[37] for TMP oxidation over Ti-MMM of 53.6 KJ/mol.

Figure 10. Arrhenius plot.

Conclusions

The present work describes wet oxidation of 2,3,5-trimethylphenol (TMP) with aqueous

hydrogen peroxide using heterogeneous M-ZSM-5 (M = Fe, H, Cu, Cr) catalysts under

mild conditions. The factors affecting the oxidation of TMP as well as their kinetic

characteristics were studied. Best catalytic results for TMP conversion and 2,3,5-

trimethyl-1,4-benzoquinone (TMBQ) yields were obtained when the reaction was

performed over Cu-ZSM-5 catalyst. So, reaction parameters were tested for this

material. Acetonitrile was found to be the best solvent for TMP oxidation because it

avoids a competitive absorption of solvent-substrate molecules over the hydrophilic

zeolite surface as occurred with protic solvents. When studying catalyst mass effect, an

optimum value of 0.1 g of Cu-ZSM-5 was determined since major quantities of catalyst

in the reaction medium produces hydrogen peroxide decomposition and a reduction in

TMP final conversion. Aqueous hydrogen peroxide was employed as oxidant since it

generates water as the only by-product. Oxidant concentration was evaluated and in

order to maximize TMBQ yields, 0.038 moles were selected because higher

concentrations promote TMP conversion but diminish TMBQ selectivity by an over

oxidation of the quinone. A combined homolytic and heterolytic mechanism is proposed

for this oxidation over Cu-ZSM-5. The optimal reaction temperature is 60 ºC to prevent

oxidant thermal decomposition. Finally, an effective Ea of 52.33 kJ/mol was also

calculated for this reaction system, indicating no diffusional limitations.

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