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

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Ind. Eng. Chem. Res., **Just Accepted Manuscript** • DOI: 10.1021/ie500852w • Publication Date (Web): 25 Jun 2014Downloaded from <http://pubs.acs.org> on June 30, 2014

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

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23 Abstract

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25 The catalytic oxidation of 2,3,5-trimethylphenol was performed over transition
26 metals modified ZSM-5 zeolites employing hydrogen peroxide as oxidant under mild
27 reaction conditions. Catalysts samples were characterized by several techniques (XRD,
28 FTIR, BET, AA) and cristallinity and orthorhombic symmetry were confirmed for all of
29 them. Best catalytic results were obtained for Cu-ZSM-5 sample, so further activity
30 studies were done over this material. 2,3,5-trimethyl-1,4-benzoquinone was obtained as
31 the main product of the selective oxidation. Reaction parameters (nature of the solvent,
32 hydrogen peroxide concentration, reaction time, catalyst mass, substrate initial
33 concentration and reaction temperature) were evaluated to reach the optimum reaction
34 conditions. According to the obtained results, an apparent activation energy of 52.33
35 kJ/mol was calculated.
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52 Keywords: 2,3,5-trimethylphenol; 2,3,5-trimethyl-1,4-benzoquinone; hydrogen
53 peroxide; Cu-ZSM-5; reaction parameters.
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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 relevance³.

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 preparation⁶.

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3 The use of hydrogen peroxide as oxidizing agent in the presence of catalysts has
4 become a clean and effective alternative among other catalytic oxidation processes and
5 is commonly named as CWPO (catalytic wet peroxide oxidation)^{7,8}. Hydrogen peroxide
6 does not produce any harmful by-products, since it just produces water. Is a nontoxic
7 reactant, improves oxidation efficiency and requires milder reaction conditions. When
8 employing homogeneous catalysts, there are two major drawbacks, namely a narrow
9 acidic pH range and the need for removing the catalyst. The use of heterogeneous
10 materials as catalysts based on low-valence transition metals appears as a promising
11 option to solve these problems, since oxidation efficiencies are relatively high and pH
12 sensitivity is lower compared with homogeneous catalysts at the same operating
13 conditions⁹.

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

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25 Copper is a common metal used in oxidation catalysis studies. As other low
26 valence transition metal ions, Cu²⁺ activates hydrogen peroxide, so many investigations
27 have been done in this field^{14,15}. There are various reports on copper-containing porous
28 and nonporous heterogeneous catalysts, which were reported to be active in the
29 selective oxidation of a variety of organic compounds in the presence of atom-efficient
30 oxidants by the well-known Fenton-type mechanism¹⁶⁻¹⁸.

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3 This work was undertaken to study the catalytic oxidation of 2,3,5-
4 trimethylphenol (TMP) to 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) with H₂O₂ using
5 transition metal modified zeolite catalysts. In one of our previous papers, the use of
6 supported K₆[CoW₁₂O₄₀]·6H₂O with Keggin structure over ZSM-5 zeolites as active
7 and selective solid catalysts for the oxidation of TMP, employing aqueous hydrogen
8 peroxide as oxidant, was reported¹⁹. However, higher yields to TMBQ were obtained
9 using Cu-ZSM-5. The use of metal-modified zeolites gave interesting results
10 considering the easiest method to obtain these materials.
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20 21 2. Experimental

22 2.1 Catalysts preparation

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25 The standard literature procedure²⁰ was employed to synthesized ZSM-5 zeolite
26 with a Si/Al molar ratio of 17. The hydrothermal crystallization was done in the Na₂O-
27 Al₂O₃-SiO₂ system, using TPAOH (Tetrapropylammonium Hydroxide) as a structure
28 directing agent. The obtained gel reached a pH > 9 and was maintained on a Teflon
29 autoclave at 120-160 °C for 10-12 days under self-generated pressure. Subsequently,
30 after the extraction of the reaction product of the reactor, it was washed with distilled
31 water and dried at 110 °C for 12 h. The structure directing agent (TPA) was desorbed in
32 N₂ atmosphere (20 ml/min) at programmed temperature (10 °C/min) from room
33 temperature to 500 °C and then it was calcined in air at 500 °C for 12 h to obtain Na-
34 HZSM-5.
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48 To obtain the NH₄⁺-form of the catalyst, the Na-zeolite was ion-exchanged with
49 NH₄Cl (1 M) solution for 40 h at 80°C. Further thermal treatments were applied to it in
50 order to obtain the protonic form of the zeolite (H-ZSM-5): desorption for 12 h in N₂
51 flow (10 ml/min) at 500°C and finally calcined in air at 500°C for 8 h.
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3 Transition metals were incorporated in the zeolite matrix by the wetness
4 impregnation method. For this purpose, the ammonium form of the zeolite was
5 suspended in an aqueous solution of the proper salt: $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Mallinckrodt), for Fe-
6 ZSM-5; $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ (Mallinckrodt), for Cu-ZSM-5 and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Fluka), for
7 Cr-ZSM-5. The water was evaporated using a rotator–evaporator at 80°C under vacuum
8 until complete dryness. Then samples were dried at 110°C and desorbed in N_2 flow at
9 500°C for 12 h, followed by calcination in air at 500°C for 8 h to obtain M-ZSM-5
10 samples.
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23 *2.2 Catalysts characterization*

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25 The content of metal in each sample was determined by Atomic Absorption in a
26 Perkin Elmer AAnalyst 800 spectrometer after the digestion of the samples by
27 microwave in a Milestone ETHOS 900 digester.
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32 Structure and cristallinity of the samples were studied by X-ray diffraction
33 patterns collected in air at room temperature in a Philips diffractometer using $\text{CuK}\alpha$
34 radiation. Diffraction data were recorded between $2\theta = 5^\circ$ and 60° at an interval of 0.05° .
35 A scanning speed of $2^\circ/\text{min}$ was used.
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40 BET surface area determinations were carried out with an ASAP 2000
41 equipment.
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45 The infrared spectra of H-zeolites and M-zeolites were recorded on a JASCO
46 5300 FTIR spectrometer. The samples were pressed into self-supporting wafers (8-10
47 mg/cm^2). Spectral scanning was done from 4600 to 400 cm^{-1} in 16 consecutive registers
48 of 4 cm^{-1} resolution each one. In order to evaluate the interaction of pyridine over
49 Lewis and Brønsted acidic sites, pyridine (3 Torr) was adsorbed at room temperature for
50 12 h and desorbed for an hour at different temperatures at 10^{-4} Torr. The experiments
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3 were carried out using a thermostated cell with CaF_2 windows connected to a vacuum
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5 line. The numbers of Brönsted and Lewis acid sites were quantified using the literature
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7 data of the integrated molar extinction coefficients²¹, resulting in no dependence of the
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9 integrated coefficients on the catalysts or strength of the sites. The FTIR spectra in the
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11 lattice vibration region ($400\text{-}1400\text{ cm}^{-1}$) were performed using KBr 0.05% wafer
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13 technique.
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16 17 18 *2.3 Catalytic activity* 19

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21 To study the oxidation of 2,3,5-trimethylphenol (99 %, Aldrich) a glass flask
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23 reactor (25 cm^3) equipped with a reflux condenser was immersed in a thermostated
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25 bath and the reaction was carried out by adding H_2O_2 aqueous solution (30 wt%,
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27 Cicarelli), confirmed by permanganometric titration. The system was constantly
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29 magnetic stirred at 1500 rpm to avoid external mass transfer resistance. The catalytic
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31 tests were performed at 60°C using 0.1 g of the catalyst and different molar ratios of
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33 TMP/hydrogen peroxide. Several solvents with different dielectric constants were
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35 tested for the reaction: acetonitrile (99.5 % Cicarelli), acetone (analytical grade,
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37 Aldrich), 2-propanol (99.5 %, Aldrich), methanol (99.5%, Cicarelli) and 2-butanol
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39 (99.5%, Merck). The reaction was monitored by taking aliquots of the reaction mixture
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41 at different reaction times. Prior to analysis, the catalyst was separated from the solution
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43 by filtration. Organic compounds were analyzed quantitatively by gas chromatography
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45 (Hewlett Packard HP-5890) with a Methyl Silicone capillary column (30m x 0.32 mm
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47 i.d) and a flame ionization detector (FID), and qualitatively, by mass spectrometry GC-
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49 Mass (Shimadzu QP 5050 GC-17 A), using a HP-S (25 m x 0.2 mm i.d) capillary
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51 column. The substrate conversion was measured as a function of reaction time and the
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53 values observed are reported as mol %.
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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	Surface area	Crystallinity	
	(%wt)	(m ² /g)	(%)	
	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 them²². Acid strength of the sites is determined according to the ability to retain

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3 pyridine as temperature is increased. Pyridine was adsorbed at room temperature over
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5 the samples and desorbed at different temperatures under vacuum for an hour.
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7 IR spectra of pyridine adsorbed on H-ZSM-5 and M-ZSM-5 samples are shown
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9 in Figure 1. Bands at $1452\text{-}1456\text{ cm}^{-1}$ (ν 19B mode) and 1612 cm^{-1} (ν 8A mode),
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11 corresponding to Py interaction with Lewis acid sites (L-Py) could be observed, as well
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13 as bands at 1547 cm^{-1} (ν 19B mode) and a shoulder at 1635 cm^{-1} (ν 8A mode), indicative
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15 of the interaction with Brönsted acid sites (PyH^+)²³. The band at $1490\text{-}1495\text{ cm}^{-1}$
16
17 corresponds to the vibration of adsorbed Pyridine over both Brönsted and Lewis acid
18
19 sites²⁴. Bands corresponding to hydrogen-bonded pyridine ($1440\text{-}1447\text{ cm}^{-1}$ and 1580-
20
21 1600 cm^{-1}) and physically adsorbed pyridine (1439 and 1580 cm^{-1})²⁵ are not
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23 considered since the spectra shown were taken after desorbed at $350\text{ }^\circ\text{C}$.
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27 H-ZSM-5 spectrum presents an important signal of Brönsted sites and some L-
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29 Py resulting from Al^{3+} . Upon introduction of metal cations in the pentasil matrix, new
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31 EDA adduct of pyridine-Lewis acid sites at 1454 cm^{-1} (O-M) were generated, stronger
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33 than the well-known Lewis aluminum acid sites of the zeolite framework (1456 cm^{-1}),
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35 since they retain more pyridine than the parent H-ZSM-5 material after outgassing at
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37 350°C . The number of Brönsted acid sites ($1545\text{-}1550\text{ cm}^{-1}$) decreases as the number of
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39 Lewis acid sites ($1450\text{-}1460\text{ cm}^{-1}$) increases for M-ZSM-5 samples.
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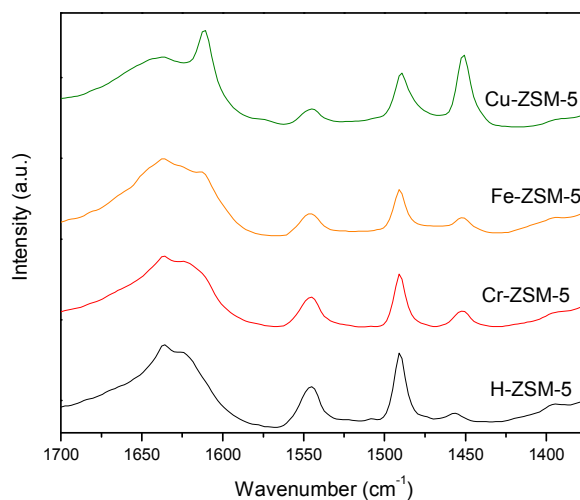


Figure 1. FTIR spectra of pyridine adsorbed at room temperature and desorbed at 350 °C and 10^{-4} Torr.

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 0.1 g 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 reaction¹⁹. 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

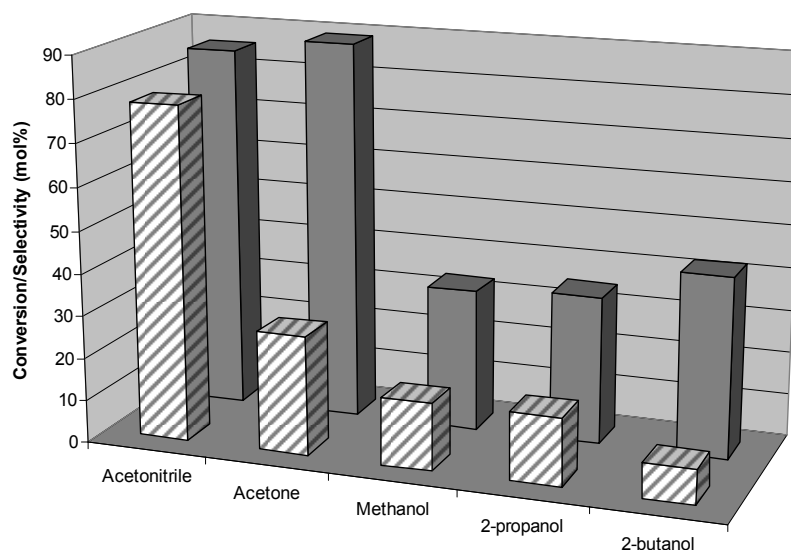
A blank experiment was performed in identical conditions, but in absence of catalyst. In this case, the oxidation reaction occurs at a very low rate, obtaining a final conversion in the order of 1 mol % after 6 h of reaction.

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

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3 since the nature of the solvent has an important effect on the outcome of the reaction
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5 considering yields, by-products formation and reaction kinetics²⁷. A series of both
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7 protic (methanol, 2-propanol, 2-butanol) and aprotic (acetonitrile, acetone) solvents were
8
9 tested for this oxidation. When studying the influence of the proticity of the solvent on
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11 TMP oxidation over Cu-ZSM-5 samples, we found that aprotic solvents give better
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13 results. As could be seen from Figure 2 and Table 3, TMP conversion values are larger
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15 for aprotic solvents and increases with Dielectric Constant values. According with
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17 Corma et al.²⁸, the enhancement on TMP conversion as the polarity of the aprotic
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19 solvents increases, could be explained by the increase of substrate concentration in the
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21 hydrophilic pores of the zeolite as Dielectric Constant values growth.
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46 Figure 2. Effect of solvent on Cu-ZSM-5 activity and selectivity to TMBQ. Symbols:

47 (▨) conversion and (■) selectivity
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Table 3. Solvents properties

Solvents	Dielectric Constant	Boiling point (°C)
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 phenoxy radicals, as found by Kholdeeva et al.²⁹.

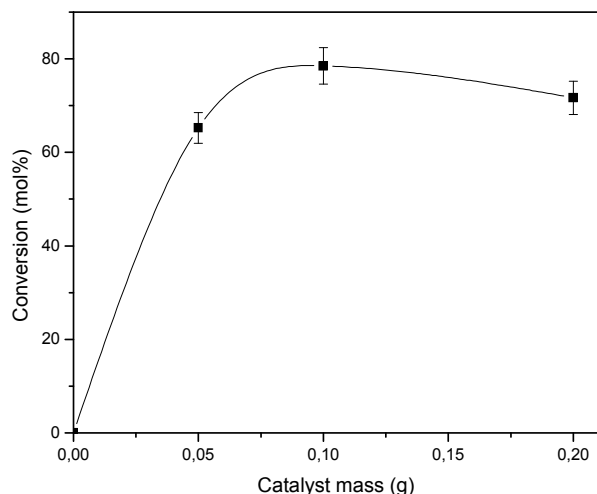
To reach better TMBQ yields, acetonitrile was chosen as the optimal solvent for TMP oxidation over Cu-ZSM-5.

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

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3 joined this increase trend until 0.1 g, then a soft decay could be observed. This tendency
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5 may be related to an auto decomposition of hydrogen peroxide that gives water and
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7 oxygen as products ($\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 0.5 \text{O}_2$)³⁰.
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9
10 It should be noted that TMBQ selectivity remain constant at every catalyst
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12 concentration evaluated, indicating that the reaction mechanism is the same in all the
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14 situations. Because of the simultaneously occurring of H_2O_2 decomposition and TMP
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16 oxidation reactions, the catalyst loading has an optimal value for obtaining the highest
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18 TMP conversion. So, since TMP conversion was considerably higher with 0.1 g of Cu-
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20 ZSM-5, our attempts to optimize reaction conditions were done employing this catalyst
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22 mass.
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43 Figure 3. Catalyst mass influence on TMP conversion
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46 Catalytic activity dependence on copper content was evaluated in the same
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48 conditions than catalyst mass evaluation but employing 0.1g of each material to ensure
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50 optimal conditions. TMP conversion results are shown in Figure 4. Catalytic activity
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52 increases as copper content up to 3 wt%, but then remains quiet constant with a slight
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54 reduction on TMBQ yield at higher copper content.
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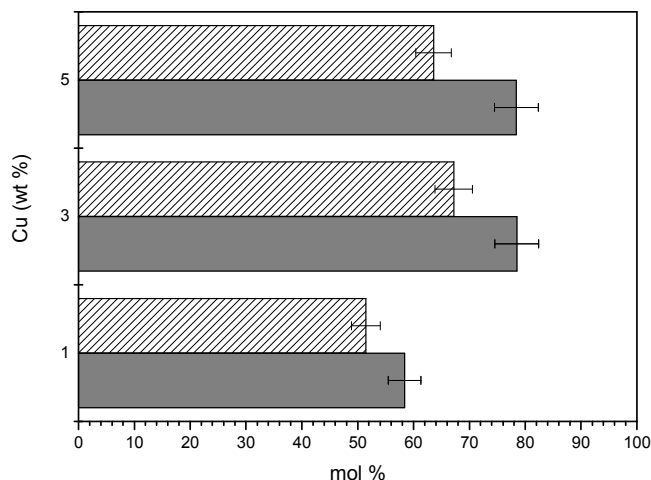


Figure 4. Dependence of TMP conversion (■) and TMBQ (▨) yield over Cu-ZSM-5 catalyst on Cu loading. Reaction conditions: Acetonitrile, as solvent, 60 °C, R=0.19.

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 °C 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.

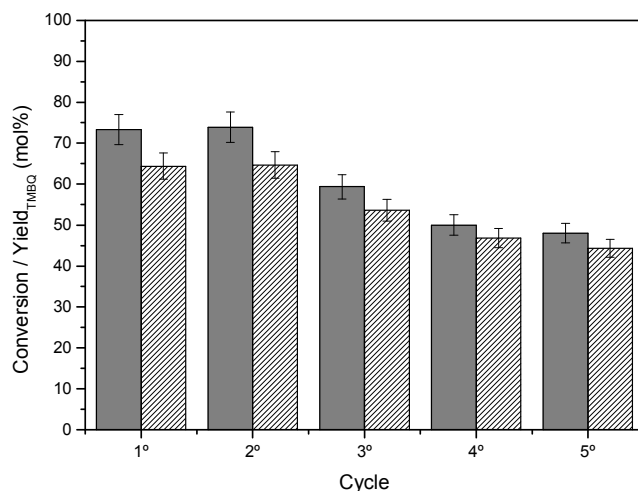


Figure 5. Stability of Cu-ZSM-5 after five cycles. TMP conversion (■) and TMBQ (▨) yield. Reaction conditions: Acetonitrile, as solvent, 60 °C, R=0.19.

3.2.4. Effect of H₂O₂ concentration

Although aqueous H₂O₂ is generally regarded as an environmentally friendly “green” reagent because it gives water as the sole by-product of oxidation³¹, the amount of hydrogen peroxide will affect the conversion of TMP and the selectivity to TMBQ. So, the effect of H₂O₂ concentration was studied at 60 °C 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 necessary³².

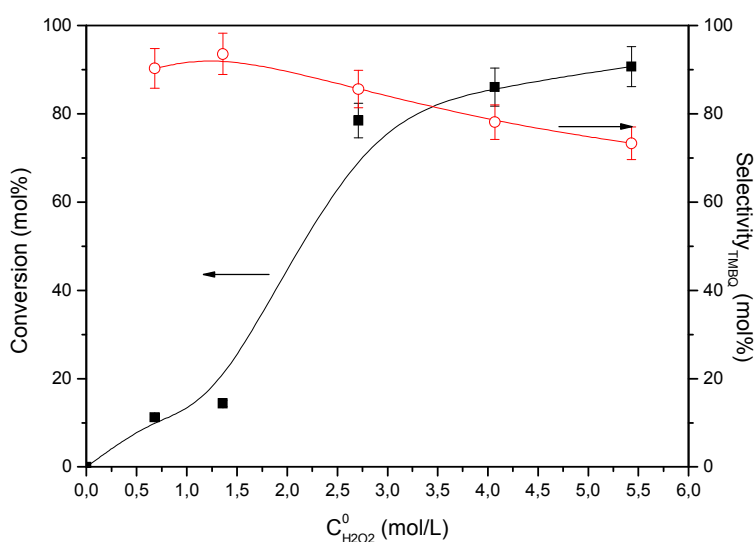
When considering oxidant concentration effect, it could be seen that two zones exists in the graph of the evolution of TMP conversion (Figure 6). Initially, conversion values goes from 11 to 79 mol% when varying hydrogen peroxide initial concentration

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 H₂O₂ for TMP oxidation was obtained. Hydrogen peroxide efficiency was calculated by the following equation:

$$Eff_{H_2O_2} = \frac{TMBQ_{obtained}(moles)}{H_2O_2_{consumed}(moles)} \times 100$$

This value is in accordance with those published by Wang et al. in styrene oxidation with hydrogen peroxide³³. 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%.



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4 Figure 6. Effect of H₂O₂ concentration on TMP conversion (■) and TMBQ selectivity
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11 To avoid the unproductive decomposition of the oxidant in the presence of the
12 Cu-ZSM-5 catalyst, oxidant was added in two steps: at the beginning of the reaction and
13 after three hours, but conversion values did not suffer considerable change.
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17 In order to get a better knowledge of the reaction mechanism, a radical
18 scavenger (isopropyl alcohol) was added after 30 minutes of reaction (Figure 7). When
19 the radical scavenger was added, TMP conversion suffers an important reduction of ~
20 30 mol%. As we proposed in our previous paper on TMP oxidation employing
21 supported heteropolycompounds as catalysts¹⁹, an homolytic mechanism previously
22 informed by Kholdeeva et al.³⁴, which includes the formation of the ArO· phenoxyl
23 radical that with further transformations results in the TMBQ, should be present in this
24 reaction system. It is well-known that Cu²⁺ activates hydrogen peroxide generating
25 hydroxyl radicals in the Fenton-like reaction, so it is possible to assume the presence of
26 a radical mechanism in this reaction system. Since no coupling dimers (biphenol,
27 polyphenylene oxide) were detected, we assume that this reaction is favored with
28 respect to the other secondary radical reactions proposed by the group of Kholdeeva.
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44 As TMHQ is obtained as the main secondary product, we propose for our
45 reaction system a combined mechanism which includes a heterolytic pathway of
46 electrophilic hydroxylation via the formation of the TMHQ^{35,36}.
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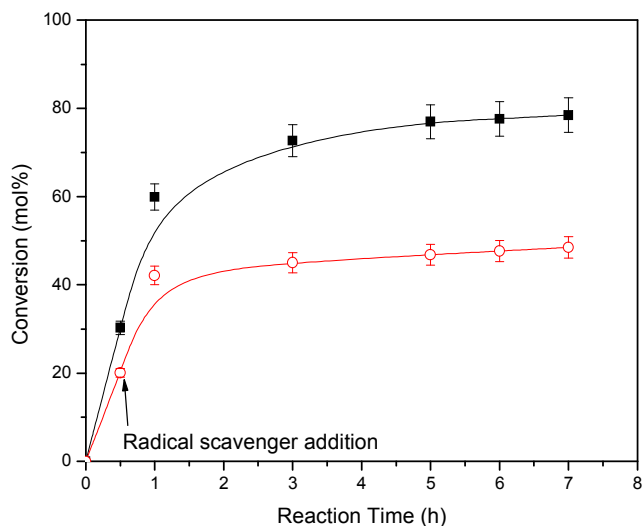


Figure 7. Effect of the introduction of a radical scavenger on TMP conversion: (■) without radical scavenger reaction; (○) adding isopropyl alcohol after 30 min. Reaction conditions: 0.1 g of Cu-ZSM-5; acetonitrile as solvent; Temperature: 60 °C.

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 °C 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.

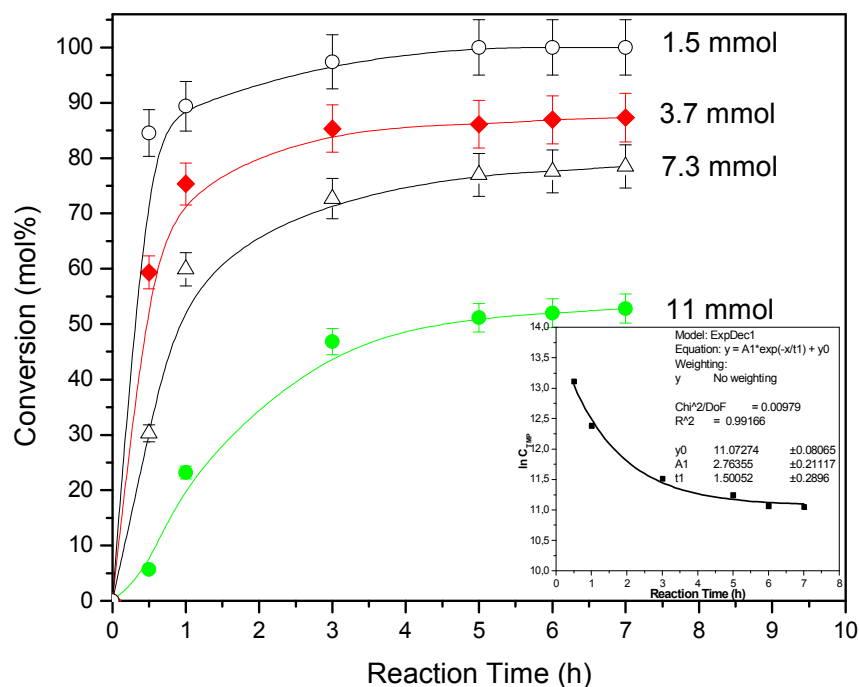


Figure 8. The reaction profile for TMP oxidation varying substrate initial concentration.

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 °C producing a lesser substrate conversion.

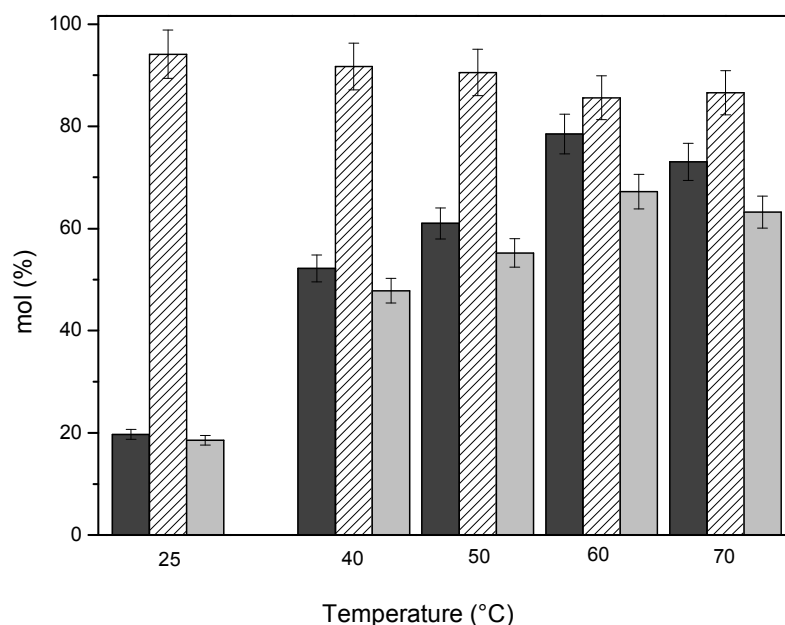


Figure 9. Effect of reaction temperature on TMP conversion, TMBQ selectivity and yield over Cu-ZSM-5. Symbols: (■) conversion, (▨) TMBQ selectivity and (■) yield.

The effective activation energy (E_a) estimated from the $\ln R_0 - 1/T$ 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 E_a 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.

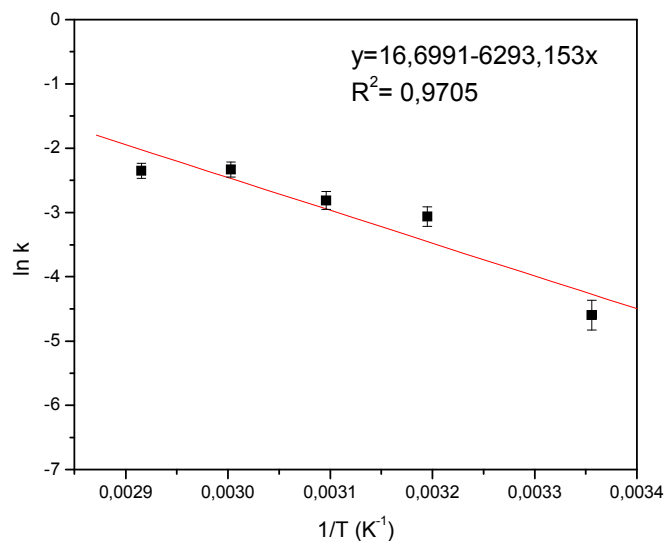


Figure 10. Arrhenius plot.

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

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3 concentrations promote TMP conversion but diminish TMBQ selectivity by an over
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5 oxidation of the quinone. A combined homolytic and heterolytic mechanism is proposed
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7 for this oxidation over Cu-ZSM-5. The optimal reaction temperature is 60 °C to prevent
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9 oxidant thermal decomposition. Finally, an effective E_a of 52.33 kJ/mol was also
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11 calculated for this reaction system, indicating no diffusional limitations.
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14 15 16 Acknowledgements

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18 This project was partially supported by: Ministerio de Ciencia y Tecnología de la
19
20 Provincia de Córdoba PID 000121, CONICET PIP 11220090100490 and UTN-PID
21
22 1275. We would also wish to thank CONICET.
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27 28 References

- 29
30 (1) Wang, F.; Ueda, W. Selective oxidation of alcohols using novel crystalline Mo-V-O
31
32 oxide as heterogeneous catalyst in liquid phase with molecular oxygen, *Catal. Today*
33
34 **2009**, *144*, 358.
35
36 (2) Coman, S.M.; Pop, G.; Stere, C.; Parvulescu, V.I.; El Haskouri, J.; Beltran, D.;
37
38 Amoros, P. New heterogeneous catalysts for greener routes in the synthesis of fine
39
40 chemicals, *J. Catal.* **2007**, *251*, 388.
41
42 (3) Rosenau, T.; Kloser, E.; Gille, L.; Mazzini, F.; Netscher, T. Vitamin E chemistry.
43
44 Studies into initial oxidation intermediates of alpha tocopherol: disproving the
45
46 involvement of 5a-C-centered "chromanol methide" radicals, *J. Org. Chem.* **2007**, *72*,
47
48 3268.
49
50 (4) Bonrath, W.; Eggersdorfer, M.; Netscher, T. Catalysis in the industrial preparation
51
52 of vitamins and nutraceuticals, *Catal. Today* **2007**, *121*, 45.
53
54
55
56
57
58
59
60

1
2
3 (5) Bonrath, W.; Netscher, T. Catalytic processes in vitamins synthesis and production,
4
5 *Appl. Catal. A* **2005**, *280*, 55.

6
7 (6) Alcón, M.J.; Corma, A.; Iglesias, M.; Sánchez, F. From homogeneous to
8
9 heterogeneous catalysis: zeolite supported metal complexes with C2-multidentate
10
11 nitrogen ligands. Application as catalysts for olefin hydrogenation and cyclopropanation
12
13 reactions, *J. Organomet. Chem.* **2002**, *655*, 134.

14
15 (7) Sotelo, J.L.; Ovejero, G.; Martinez, F.; Melero, J.A.; Milieni, A. Catalytic wet
16
17 peroxide oxidation of phenolic solutions over a LaTi_{1-x}Cu_xO₃ perovskite catalyst,
18
19 *Appl. Catal. B* **2004**, *47*, 281.

20
21 (8) Zrncevic, S.; Gomzi, Z. CWPO: An Environmental Solution for Pollutant Removal
22
23 from Wastewater, *Ind. Eng. Chem. Res.* **2005**, *44*, 6110.

24
25 (9) Inchaurredo, N.S.; Massa, R.; Fenoglio, J.; Font, P.; Haure. Efficient catalytic wet
26
27 peroxide oxidation of phenol at moderate temperature using a high-load supported
28
29 copper catalyst, *Chem. Eng. J.* **2012**, *198–199*, 426.

30
31 (10) Timofeeva, M.N.; Khankhasaeva, S.Ts.; Talsi, E.P.; Panchenko, V.N.; Golovin,
32
33 A.V.; Dashinamzhilova, E.Ts.; Tsybulya, S.V. The effect of Fe/Cu ratio in the synthesis
34
35 of mixed Fe,Cu,Al-clays used as catalysts in phenol peroxide oxidation, *Appl. Catal. B*
36
37 **2009**, *90*, 618.

38
39 (11) Zhou, S.; Qian, Z.; Sun, J.; Xu, C.; Xia, V. Catalytic wet peroxide oxidation of
40
41 phenol over Cu–Ni–Al hydrotalcite, *Appl. Clay Sci.* **2011**, *53*, 627.

42
43 (12) Čejka, J.; Centi, G.; Perez-Pariente, J.; Rotha, W. Zeolite-based materials for novel
44
45 catalytic applications: Opportunities, perspectives and open problems, *Catal. Today*
46
47 **2012**, *179*, 2.

- 1
2
3 (13) Sashkina, K.A.; Labko, V.S.; Rudina, N.A.; Parmon, V.N.; Parkhomchuk, E.V.
4 Hierarchical zeolite FeZSM-5 as a heterogeneous Fenton-type catalyst, *J. Catal.* **2013**,
5 *299*, 44.
6
7
8
9 (14) Gil, A.; Korili, S.A.; Trujillano, R.; Vicente, M.A. (Eds.), Pillared Clays and
10 Related Catalysts, Springer, **2010**.
11
12 (15) Caudo, S.; Centi, G.; Genovese, C.; Perathoner, S. Homogeneous versus
13 heterogeneous catalytic reactions to eliminate organics from waste water using H₂O₂, *J.*
14 *Top. Catal.* **2006**, *40*, 207.
15
16 (16) Handique, J.G.; Baruah, J.B. The oligomer of 1,6-naphthalenediol as a support in
17 oxidative reactions of cis-bisglycinato copper(II) and hydrogenperoxide, *J. Molec.*
18 *Catal.* **2001**, *172*, 19.
19
20 (17) Kato, C.N.; Hasegawa, M.; Sato, T.; Yoshizawa, A.; Inoue, T.; Mori, W.
21 Microporous dinuclear copper(II) trans-1,4-cyclohexanedicarboxylate: heterogeneous
22 oxidation catalysis with hydrogen peroxide and X-ray powder structure of peroxo
23 copper(II) intermediate, *J. Catal.* **2005**, *230*, 226.
24
25 (18) Tsai, C.L.; Chou, B.; Cheng, S.; Lee, J.F. Synthesis of TMBQ using Cu(II)-
26 substituted MCM-41 as the catalyst, *Appl. Catal. A* **2001**, *208*, 279.
27
28 (19) Saux, C.; Pizzio, L.; Pierella, L. 2,3,5-Trimethylphenol oxidation over Co-based
29 solid catalysts, *Appl. Catal. A* **2013**, *452*, 17.
30
31 (20) Chu, P. US Patent No. 3.709.979 **1972**.
32
33 (21) Emeis, C. A. Determination of Integrated Molar Extinction Coefficients for
34 Infrared Absorption Bands of Pyridine Adsorbed on Solid Acid Catalysts, *J.*
35 *Catal.* **1993**, *141*, 347.
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (22) Busca, G. The surface acidity of solid oxides and its characterization by IR
4 spectroscopic methods. An attempt at systematization, *Phys. Chem.* **1999**, *1*, 723.
5
6
7 (23) Rhee, K.; Rao, U.; Stencil, J.; Melson, G.; Crawford, J. Supported transition
8 metal compounds: Infrared studies on the acidity of Co/ZSM-5 and Fe/ZSM-5 catalysts,
9 *Zeolites* **1983**, *3*, 337.
10
11
12 (24) Borade, R.; Sayari, A.; Adnot, A.; Kaliaguine, S. Characterization of acidity in
13 ZSM-5 zeolites: an x-ray photoelectron and IR spectroscopy study, *J. Phys. Chem.*
14 **1990**, *94*, 5989.
15
16
17 (25) Pérez-Ramírez, J.; Groen, J. C.; Bückner, A.; Kumar, M. S.; Bentrup, U.; Debbagh,
18 M. N.; Villaescusa, L. A. Evolution of isomorphously substituted iron zeolites during
19 activation: comparison of Fe-beta and Fe-ZSM-5, *J. Catal.* **2005**, *232*, 318.
20
21
22 (26) Pierella, L.; Saux, C.; Caglieri, S.; Bertorello, H.; Bercoff, P. Catalytic activity and
23 magnetic properties of Co-ZSM-5 zeolites prepared by different methods, *Appl. Catal.*
24 *A* **2008**, *347*, 55.
25
26
27 (27) Hulea, V.; Dumitriu, E. Styrene oxidation with H₂O₂ over Ti-containing molecular
28 sieves with MFI, BEA and MCM-41 topologies, *Appl. Catal. A* **2004**, *277*, 99.
29
30
31 (28) Corma, A.; Esteve, A. Martinez. Solvent Effects during the Oxidation of Olefins
32 and Alcohols with Hydrogen Peroxide on Ti-Beta Catalyst: The Influence of the
33 Hydrophilicity–Hydrophobicity of the Zeolite, *J. Catal.* **1996**, *161*, 11.
34
35
36 (29) Kholdeeva, O.; Ivanchikova, I; Guidotti, M.; Ravasio, N.; Sgobba, M.; Barmatova,
37 M.; How to reach 100% selectivity in H₂O₂-based oxidation of 2,3,6-trimethylphenol
38 to trimethyl-p-benzoquinone over Ti,Si-catalysts, *Catal. Today* **2009**, *141*, 330.
39
40
41 (30) Choudhary, V. R.; Patil, N. S.; Chaudhari, N. K.; Bhargava, S. K. Epoxidation of
42 styrene by anhydrous hydrogen peroxide over boehmite and alumina catalysts with
43 continuous removal of the reaction water, *J. Molec. Catal. A* **2005**, *227*, 217.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (31) Li, P.; Zhang, M.; Wu, M.; Liu, W.; Yi, Z.; Yang, M.; Zhang, J.; Zhang, G.; Bai, Z.
4
5 An effective oxidation of 2,3,6-trimethylphenol to 2,3,5-trimethylbenzoquinone using
6
7 Fenton's reagent under mild conditions, *Chem. Eng. J.* **2009**, *146*, 270.
8
9
10 (32) Palacio M., Villabrile P., Romanelli G., Vazquez P., Cáceres C., Preparation,
11
12 characterization and use of V₂O₅-TiO₂ mixed xerogels as catalysts for sustainable
13
14 oxidation with hydrogen peroxide of 2,3,6-trimethylphenol, *Appl. Catal. A* **2012**, *417*-
15
16 *418*, 273.
17
18 (33) Wang, Y.; Zhang, Q.; Shishido, T.; Takehira, K. Characterizations of Iron-
19
20 containing MCM-41 and its catalytic properties in epoxidation of Styrene with
21
22 hydrogen peroxide, *J. Catal.* **2002**, *209*, 186.
23
24
25 (34) Kholdeeva, O.A.; Golovin, A.V.; Maksimovskaya R.I., Kozhevnikov I.V.,
26
27 Oxidation of 2,3,6-trimethylphenol in the presence of molybdovanadophosphoric
28
29 heteropoly acids, *J. Molec. Catal.* **1992**, *75*, 235.
30
31
32 (35) Trukhan, N., Kholdeeva, N. Kinetics and Mechanism of 2,3,6-Trimethylphenol
33
34 Oxidation by Hydrogen Peroxide in the Presence of TiO₂-SiO₂ Aerogel, *Kinet. Catal.*
35
36 **2003**, *44*, 347.
37
38 (36) Li, Y.; Liu, W.; Wu, M.; Yi, Z.; Zhang, J. Oxidation of 2,3,5-trimethylphenol to
39
40 2,3,5-trimethylbenzoquinone with aqueous hydrogen peroxide in the presence of spinel
41
42 CuCo₂O₄, *J. Molec. Catal. A* **2007**, *261*, 73.
43
44
45 (37) Trukhan, N.N.; Romannikov, V.N.; Paukshtis, E.A.; Shmakov, A.N.; Kholdeeva,
46
47 O.A. Oxidation of 2,3,6-Trimethylphenol over Ti- and V-Containing Mesoporous
48
49 Mesophase Catalysts: Structure-Activity/Selectivity Correlation, *J. Catal.* **2001**,
50
51 *202*, 110.
52
53
54
55
56
57
58
59
60