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Synthesis of menadione over selective oxidation zeolites

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Abstract

We report on the synthesis of Menadione (vitamin K_3) by selective oxidation of 2-methylnaphthalene (2MN) with hydrogen peroxide over Ti- and Fe-containing catalysts. Different parameters affecting the oxidation of 2-methylnaphthalene with hydrogen peroxide on zeolite Fe-Beta are described. The influence of the amount of catalyst as well as the concentration of hydrogen peroxide and the influence of the reaction temperature on the reaction rate were studied. The effect of the nature of the solvent was also investigated. All tests were performed over several selective oxidation zeolitic catalysts, synthesized and characterized in our laboratory.

Keywords: Vitamin K_3 synthesis; Oxidation catalysts; Zeolites materials; Kinetic study

1. Introduction

2-Methyl-1,4-naphthoquinone, used therapeutically under the name of Menadione, was found to have more antibleeding activity than the natural vitamins K_1 or K_2.

The empirical formula of Menadione is $C_{11}H_8O_2$. Menadione occurs as a bright-yellow crystalline powder and is almost odorless. It is insoluble in water but soluble in vegetable oils, acetone and benzene and is sparingly soluble in alcohol and in chloroform. It is affected by sunlight. Menadione powder is irritant to the skin and to the respiratory tract.

In the course of the catalytic vitamin K cycle, this vitamin is reduced to vitamin KH_2 by an enzyme reductase. Vitamin KH_2 is then transformed to vitamin K oxide as the carboxylation of glutamate is effected to γ-carboxyglutamate [1]. In a recent paper Dowd et al. [1] working with 2-methyl-3-phytyl-1,4-naphthoquinone, the bloodclotting vitamin K_1, demonstrated that the oxygenation (to form vitamin K oxide) takes place adjacent to the methyl group. Accordingly, this position can be designated the active site of vitamin K_1. Taking into account these new findings, the synthesis of vitamin K_3 (2-methyl-1,4-naphthoquinone) is raising great interest because it has about three times more antibleeding activity than vitamin K_1.

In a well known process, 2-methylnaphthalene is oxidized with a sulfuric acid solution of chromic acid to give the vitamin in 38 to 42% yield [2]. In this process, much effort is given to the treatment of wastewater. Therefore,

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some reaction systems using hydrogen peroxide in the presence of acid catalysts have been claimed in patents [3–5]. Recently, the oxidation has been carried out using ammonium persulfate as an oxidizing agent in the presence of cerium (IV) ammonium sulfate and silver nitrate in an emulsified solution [6]. However, a more convenient and effective reaction system using solid catalyst has been proposed by Yamaguchi et al. [7]. They found that Pd (II) acetate fixed on polystyrene sulfonic acid resin effectively catalyzes the oxidation of 2-methyl naphthalene to 2-methyl-1,4-naphthoquinone with aqueous hydrogen peroxide as oxidant and acetic acid as solvent.

Recently we reported the selective synthesis of 2-methylnaphthalene by alkylation of naphthalene with methanol [8] and by transalkylation of naphthalene with mesitylene [9] over MEL zeolites with protons as active centers. In this paper we report on the selective synthesis of 2-methyl-1,4-naphthoquinone by oxidation of 2-methylnaphthalene with hydrogen peroxide over selective oxidation zeolites.

2. Experimental

2.1. Catalyst preparation

All the samples were prepared by the sol–gel method using raw amorphous SiO_2/Hetero-atomO_2 xerogels [10]. The following reactants were used: TEOS (TetraEthyl OrthoSilicate) as source of silicon. TiPOT (TetraisoPropyl OrthoTitanate) and TnBOT (TetraButyl OrthoTitanate) as raw material for titanium. Ferric nitrate as source of iron. TPAOH (TetraPropylAmmonium Hydroxide) and TBAOH (TetraButyl Ammonium Hydroxide) as template for TS-1; TEAOH (TetraEthylAmmonium Hydroxide) for TiBEA; DTMA (DodecylTriMethylammonium Bromide) for MCM-41 and HMTBOH(N,N'-Hexamethylenebis [tributylammonium hydroxide]) for NCL-1 zeolite. Xerogels of SiO_2/TiO_2 and SiO_2/Fe_2O_3 solid were used as raw material.

The final products were filtered, washed with distilled water, dried at 110°C and calcined at 500°C for 12 h. The zeolites obtained were: TS-1[a], Fe-Si[b], Ti-BEA[c], Fe-BEA[d], Ti-NCL-1[e], Ti-MCM-41[f], [11].

2.2. Catalyst characterization

The powder XRD patterns with applications of Synchrotron radiation was performed in the Laboratorio Nacional de Luz Sincrotron, LNLS/CNPq, Campinas, SP-Brazil. Surface area BET determinations were collected with an ASAP 2000 equipment. The metal content of the catalysts was determined by XRF. The concentration of the metal in solution after the oxidation reaction was determined by complexometric titration with EDTA and salicilic acid as indicator. Infrared analysis of the catalysts was performed on a JASCO 5300 spectrometer in the lattice vibration region using KBr 0.05% wafer technique. Pyridine adsorption experiments were carried out in a thermostatized cell with CaF_2 windows connected to a vacuum line, and a self-supporting wafer was used. TPD data were collected with an INSTRELEC programmer, which allows to change the heat slope. The slope was 10–20°C/min and nitrogen flow of 20 ml/min. Desorbed products were analyzed using a FID detector.

2.3. Catalytic activity

The standard reactions of oxidation of 2-methylnaphthalene (Aldrich 98.9%) to 2-methyl-1,4-naphthoquinone were performed in a Teflon batch reactor (autoclave), varying the reaction times, temperatures, oxidant-substrate and catalyst-substrate ratios. Acetone (Cicarelli 99%) was used as solvent and hydrogen peroxide 30% as oxidant. Blank reactions were performed in the same way as standard reaction with the exception that no catalyst as added.

The products were filtered and analyzed by high-performance liquid chromatography (HPLC) in a JASCO PU 980 chromatograph, using the standard internal method with a M and S Pack (C18) column using MeOH–H_2O (Optima Fisher HPLC grade)(100:15) as eluent. HPLC conditions: flow rate: 1 ml/min, P_{max}: 350 kg/cm^2, $P_{min} = 0$ kg/cm^2, detector ultraviolet at 245 nm, ultraviolet spectroscopy in a JASCO UV–VIS 78000 and GC-Mass spectroscopy using GCMS-730 b. H_2O_2 present in the solution at the end of the reaction was determined by iodometric titration.

3. Results and discussion

The IR spectra of the catalysts indicated good crystallinity taking into account the ratio of intensity at 550/450 cm^{-1} for the samples [a] and [b], 572–521/468–430 for [c] and [d], 540/468 for [e] and 575/430 cm^{-1} for the sample [f]. In function of the ratio of intensity at 960–970.8/800, the Si/Ti ratios were: [a] = 50, [c] = 45, [e] = 33, [f] = 25. Surface areas BET were: [a] = 412, [b] = 400, [c] = 370, [d] = 398, [e] = 396 and [f] = 870 m^2/g. X-ray diffraction analysis with Synchrotron radiation confirmed the crystallinity of the samples $> 95\%$ and lack of phases as anatase, rutile or christobalite. TPD analyses of Templates used in the catalyst syntheses, which maximum speed of leakage of mass reaches 413–465°C, also confirm the sample crystallinity. Templates TPD, used in the amorphous xerogels preparation for the materials, indicated lower interaction energy between the organic bases in the amorphous materials (maximum speed of leakage of mass between (300–310°C) than in crystalline materials.

The results of blank reactions indicated that only 0.5% of 2-methylnaphthalene (2MN) is converted, with 10% of selectivity to 2-methyl-1,4-naphthoquinone even in the presence excess of H_2O_2.

Table 1 shows the results of catalytic activity and selectivity and H_2O_2 decomposition (conversion and selectivity to oxigenate–naphthalene derivatives), in standard conditions for the synthesized catalysts. From the data in Table 1, the Fe-BEA sample is active and selective for the synthesis of vitamin K_3 with higher peroxide selectivity.

The leaching of Fe^{3+} cations out of zeolites or amorphous silica depends strongly on the pH. Fajerwerg and Debellefontaine [12] studied the influence of the pH in wet oxidation of phenol by hydrogen peroxide over heterogeneous catalysts. They concluded that in order to minimise the iron concentration in the solution and to promote phenol degradation, the pH values set above 3.5. In our case, we do not find Fe^{3+} in solution at the end of the reaction. The pH of

Table 1
Conversion and product selectivity over different catalysts in standard conditions: Cat = 100 mg, T = 100°C, H_2O_2 = 6 ml, 2MN = 1 g, t = 4 h

Catalyst	Ti,Fe[a] (mol%)	2MN conversion (mol%)	H_2O_2 conversion/ selectivity[b](mol%)	Product selectivity (mol%)		
				1OH-2MN	1,4DOH-2MN	2M-1,4NQ
TS-1	1.81	10	15/58	34	11	55
Ti-Beta	1.80	11	16/60	34	3	63
TiMCM-41	1.82	28	38/64	55	10	35
Ti-NCL-1	1.70	8	16/44	30	3	67
Fe-Si	1.12	17	21/71	31	5	64
Fe-Beta	1.32	22	23/84	45	1	54

[a] Ti,Fe mol% in calcined sample.
[b] Selectivity in the use of H_2O_2 towards the formation of oxygenated naphthalene derivates.
1OH-2MN (1-hydroxy-2methylnaphthalene); 1,4DOH-2MN(1,4-dihydroxy-2-methylnaphthalene), 2-M-1,4NQ(2-methyl-1,4-naphthoquinone).

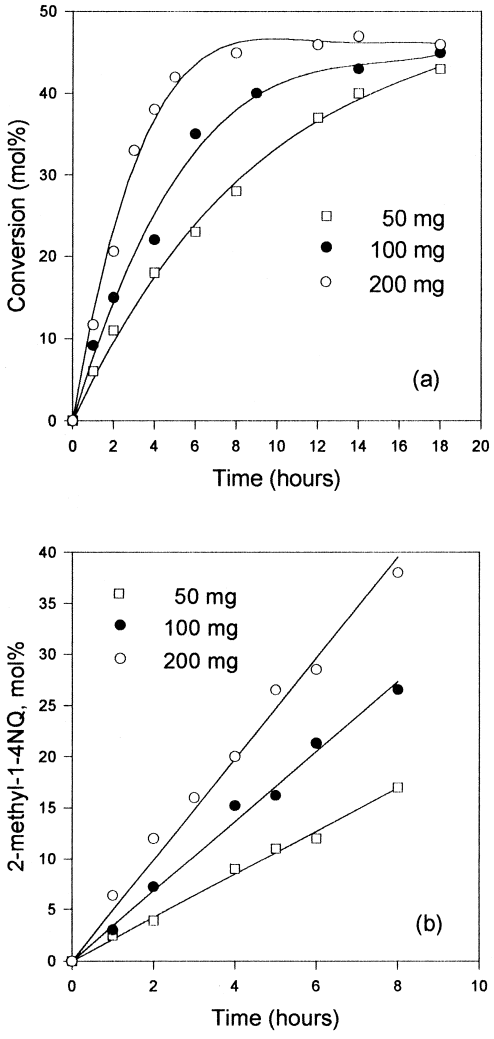

Fig. 1. Influence of the amount of catalyst Fe-Beta on the oxidation of 2-methylnaphthalene (a) Conversion vs. time (b) Yield vs. time. Cat = 100 mg, $T = 100°C$, $H_2O_2 = 6$ ml, 2MN = 1 g, $t = 4$ h.

the solution was 5 and consequently, the activity of Fe-zeolites catalysts employed in the oxidation of 2MN using H_2O_2 as oxidant is a heterogeneous phenomenon. Analysis of the titanium content of the catalysts by XRF allow one to quantify the loss of titanium from the catalysts. Only Ti-MCM-41 catalyst showed a modest lost of titanium [13]. With the other Ti-containing zeolites the Ti leaching was negligible.

To obtain mechanistic information about the oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone with hydrogen peroxide, we took into account the effect of amount of catalyst, hydrogen peroxide concentration and the reaction temperature at different times.

3.1. Influence of the amount of catalyst

The oxidation of 2-methylnaphthalene was studied under standard conditions with the exception that the amount of catalyst was changed from 50 to 100 and 200 mg in each reaction. The results of these experiments (Fig. 1) showed that the initial reaction rate increases almost linearly with increasing amount of catalyst, suggesting a first-order dependence.

3.2. Influence of hydrogen peroxide concentration

In Fig. 2, the conversion of 2-methylnaphthalene vs. time is displayed for three different hydrogen peroxide concentrations. A linear increase in the initial reaction rate with increasing hydrogen peroxide content is observed, which means that the 2-methyl naphthalene oxidation is first order in oxidant concentration. The max-

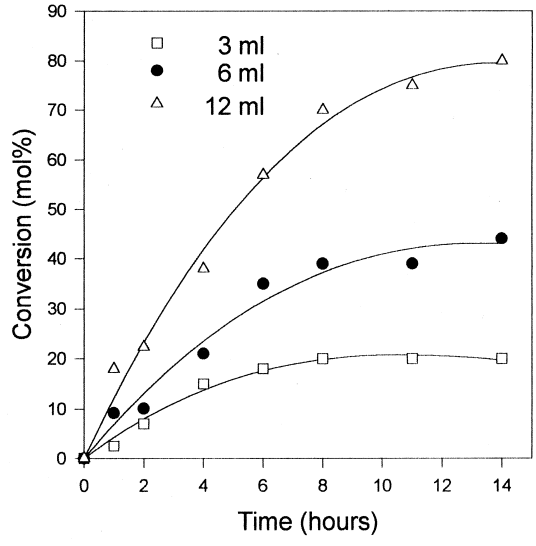

Fig. 2. Influence of the hydrogen peroxide concentration on the oxidation of 2-methylnaphthalene over Fe-Beta. Cat = 100 mg, $T = 100°C$, 2MN = 1 g, $t = 4$ h.

imum conversion was proportional to the hydrogen peroxide concentration.

Thus the overall reaction rate for the oxidation of 2-methyl naphthalene can be described by the following equation:

$$\gamma = k[\text{cat}]^1[\text{H}_2\text{O}_2]^1 \quad (1)$$

which, for a constant amount of catalyst, can be simplified to the following first-order rate equation:

$$\gamma = k'[\text{H}_2\text{O}_2]^1 \quad (2)$$

Thus, the following relation between the relative conversion X and the reaction time t can be derived:

$$\ln(1 - X) = -k't \quad (3)$$

Plotting $\ln(1 - X)$ versus time, from the slope of this curve can be obtained the value of the first-order rate constant k', which can be used to characterize the catalyst activity.

3.3. Influence of reaction temperature

The influence of the reaction temperature in the range 80–120°C on the oxidation of 2-methylnaphthalene is shown in Fig. 3. From the curves, the value of k' can be obtained for each temperature by application of equation [3], where k' is the slope of each plot (Fig. 4).

An Arrhenius plot of the first-order reaction rate constant obtained from these conversion curves is shown in Fig. 5.

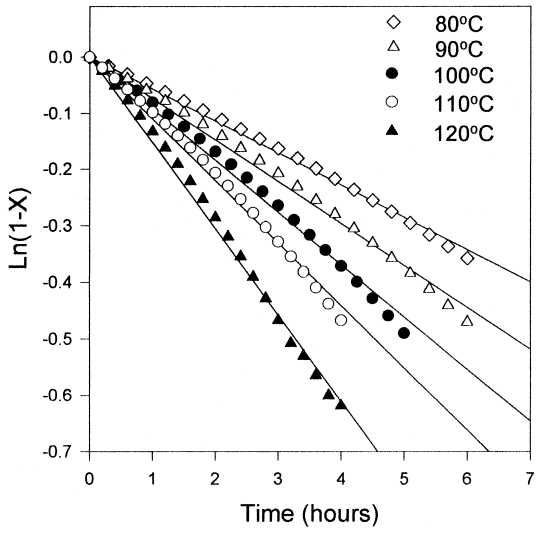

Fig. 4. First-order relationship between relative conversion X and reaction time.

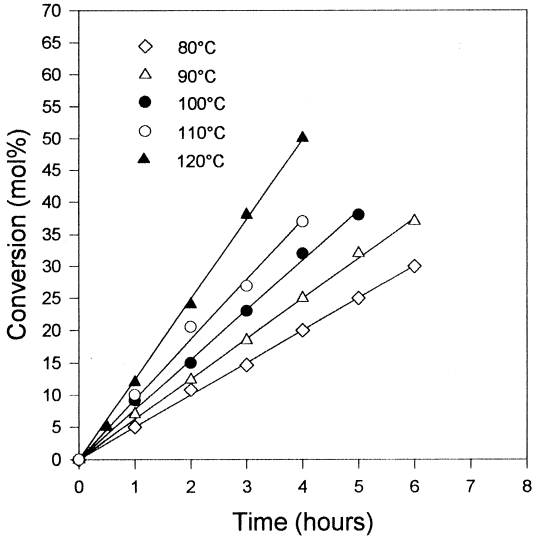

Fig. 3. Influence of the reaction temperature on the conversion of 2-methylnapthalene. Cat = 100 mg, H_2O_2 = 6 ml, 2MN = 1 g, t = 4 h.

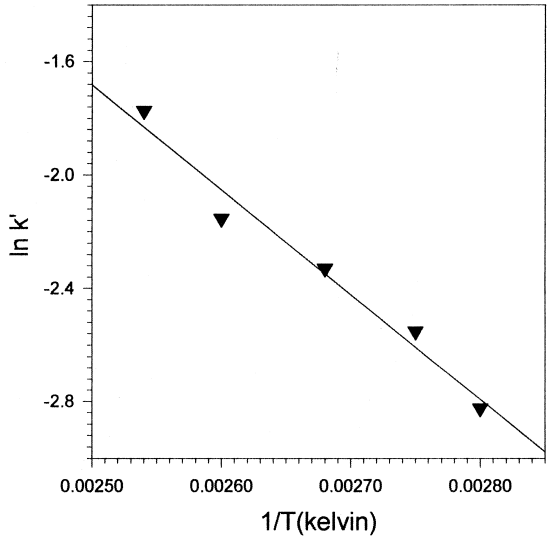

Fig. 5. Arrhenius plot of the first-order rate constant for the oxidation of 2-methylnaphthalene.

Table 2
Conversion, selectivity and yield using different solvents. Cat = 100 mg, $T = 100°C$, $H_2O_2 = 6$ ml, 2MN = 1 g, $t = 4$ h

Solvent	Dipolar moment (Debye)	Conv. (mol%)	Select. (mol%)	Yield (mol%)
Acetone	2.88	22	54	11.88
Acetonitrile	3.92	23.56	39.05	10.74
Methanol	1.70	2.87	31.39	0.91
Ethanol	1.68	6.65	12.11	1.69
Water	1.87	5.57	33.73	1.95

According to the Arrhenius equation, $\ln k' = -E/RT + \ln A_o$, the slope of the curve gives the value of E/R, which leads to an activation energy for this reaction of 30.62 kJ/mol.

3.4. Influence of the nature of the solvent

The standard reaction was carried out with the solvents acetone, acetonitrile, methanol, ethanol and water and the results are shown in Table 2. It can be observed that better yield is obtained with polar solvents, so acetone and acetonitrile are adequate solvents for the oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone.

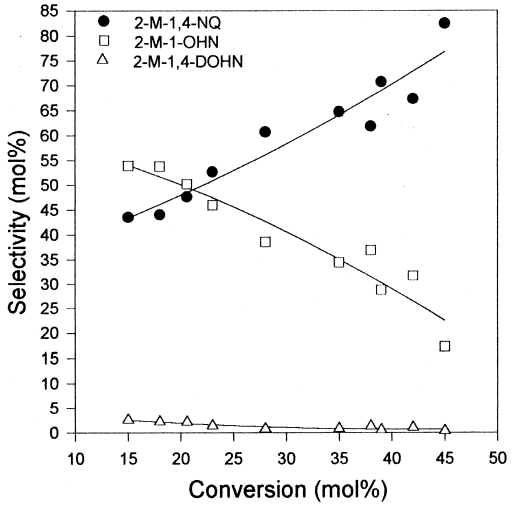

Fig. 6. Product selectivity as a function of 2-methylnaphthalene conversion (Cat = 50, 100, 200 mg, $H_2O_2 = 6$ ml, 2MN = 1 g, $T = 100°C$ and at different reaction time).

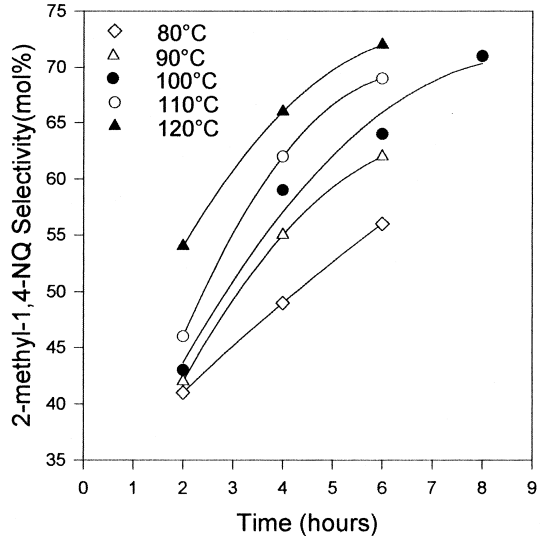

Fig. 7. Product selectivity as a function of reaction time at different reaction temperatures (Cat = 100 mg, $H_2O_2 = 6$ ml, 2MN = 1 g).

3.5. Selectivity of Fe-Beta Catalyst

The product selectivity of Fe-Beta zeolite as a function of 2-methylnaphthalene conversion is showed in Fig. 6. There it can be seen that the selectivity for 2MNQ increase with the conversion. As the formation of quinone occurs through consecutive (but very fast) steps, their yield increases as the conversion 2-methylnaphthalene increases. Very fast decreasing of naphthol derivatives selectivity was achieved, reaching to 15% at 45% of 2-methylnaphthalene conversion, whereas VK3 selectivity reach 83%. In Fig. 7 we can see the benefit effect of the reaction temperature on VK3 selectivity, showing the higher activation energy in their synthesis.

4. Conclusion

The results presented here indicate the feasibility to develop a catalytic system (substrate-catalyst-reactor-operative conditions) competi-

tive for the synthesis of Menadione using selective oxidation zeolites, acetone as solvent and hydrogen peroxide as oxidant.

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