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Catalysis Today 121 (2007) 58–64
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New routes to Vitamin K_3

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Abstract

New clean and efficient methods for the production of 2-methyl-1,4-naphthoquinone (MNQ, menadione, Vitamin K_3) based on the oxidation of 2-methyl-1-naphthol (MNL) with cheap and environmentally benign oxidants, aqueous hydrogen peroxide, *tert*-butyl hydroperoxide and molecular oxygen, using three types of true heterogeneous catalysts, such as hydrothermally stable mesoporous titanium-silicate Ti-MMM-2, silica supported iron phthalocyanine and supported gold nanoparticles, are reported. Advantages and drawbacks of the catalytic systems are discussed. Surprisingly, non-catalytic oxidation of MNL with molecular oxygen shows superior selectivity and volume yield of MNQ compared to the known catalytic methods.

Keywords: 2-Methyl-1-naphthol; 2-Methyl-1,4-naphthoquinone; Menadione; H_2O_2; Molecular oxygen; *Tert*-butyl hydroperoxide

> “All human work and thinking takes the way from primitive through complicated to the very simple.”
>
> Antoine de Saint-Exupery (Taken from the lecture of M. Beller, 10 June 2002, Turku)

1. Introduction

Vitamin K_3 (2-methyl-1,4-naphthoquinone, MNQ, menadione) is widely used as a blood coagulating agent and is a key intermediate in the preparation of the other vitamins of group K (Scheme 1) [1–3].

Industrially, menadione is produced (~1500 t/year) *via* stoichiometric oxidation of 2-methylnaphtalene (MN) with CrO_3 in sulfuric acid with moderate yields (40–50%) [2–6]. This process is a typical example of a ‘dirty’ fine chemical industry process leading to a huge amount of waste (*E*-factor is above 18) [4,5]. Other stoichiometric approaches also produce significant amounts of waste and/or demand drastic conditions. The combination of 10 mol% CrO_3 with 5 equiv. of H_5IO_6 provided 61% yield of MNQ [7]. MN was oxidized to MNQ by [bis(trifluoroacetoxy)]iodobenzene (1.5 equiv.), *tert*-butyl hydroperoxide (TBHP, 5 equiv.) and $NaHCO_3$ (5 equiv.) with the yield of 55% [8]. Recently the oxidation of MN was proposed by H_2O_2 (50–80%) in the presence of carboxylic acids, their respective anhydrides and a strong mineral acid (H_2SO_4 or $HClO_4$) to give MNQ with yield of 40–80% [9]. The development of cleaner, catalytic methods for the synthesis of menadione is therefore a challenging goal. Several catalytic procedures based on the oxidation of MN were reported (Table 1) [7–21]. In general, the selectivity is moderate due to formation of numerous side-products (Scheme 2), the main one being isomeric 6-methyl-1,4-naphthoquinone (6-MNQ).

Significantly, the oxidation of the more activated substrate, 2-methyl-1-naphthol (MNL), instead of MN allows one to increase selectivity to MNQ because formation of some by-products, in particular, 6-MNQ and oxidation products of methyl group, is avoided in this case.

The development of efficient catalytic methods for the production of MNL from 1-naphthol or 1-tetralone allows one to view this substrate as available starting material for the production of menadione [22–24]. Chelate cobalt complexes were reported to catalyze oxidation of MNL with molecular oxygen [25]; however, poorly described experimental details

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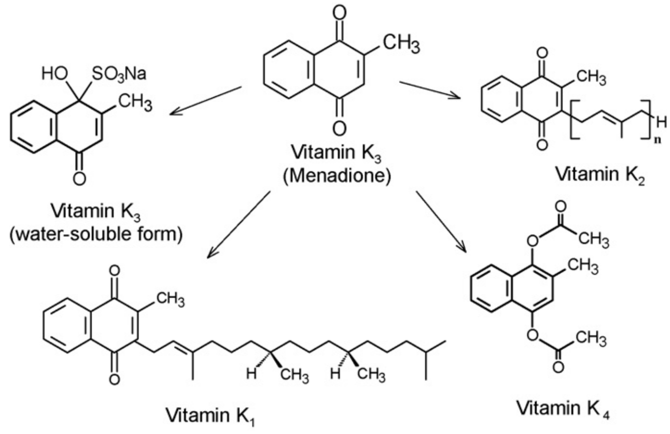
doi:10.1016/j.cattod.2006.11.011



Scheme 1. Vitamins of group K.

Table 1
Catalytic oxidations of 2-MN

Catalyst	Oxidant	Selectivity (%)	Conversion (%)	Reference
Ce(IV)	$(NH_4)_2S_2O_8$	67	94	[18]
Ru(III)	$(Cr_2O_7)^{2-}$	90	27	[19]
Mn and Fe-porphyrines	$KHSO_5$	53	86	[20,21]
	AcOOH	62	100	
CrO_3	H_5IO_6	65	99	[7]
CH_3ReO_3	H_2O_2	58	81	[10,11]
Pd(II)	H_2O_2	66	90	[15]
Fe(III)	H_2O_2	36	95	[12]
Fe-phthalocyanine	TBHP	45	70	[13]
Ti- and Fe-containing mol. sieves	H_2O_2	54	22	[16,17]

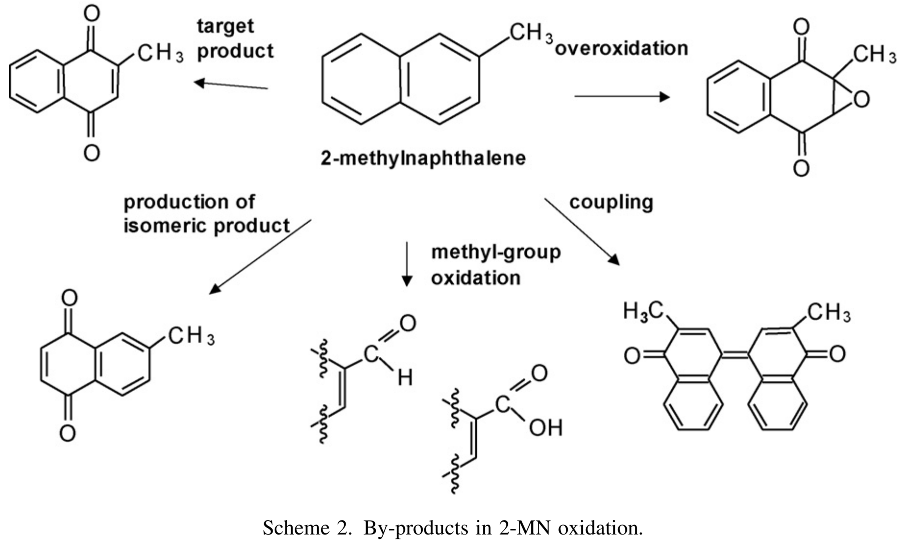
do not allow one to reproduce the results. In 1994, Matveev et al. suggested Keggin type phosphomolibdovanadium heteropoly acids/acid salts (V-HPA) as reversibly acting oxidants ([V-HPA]/[MNL] > 1) to convert MNL to MNQ [26–29]. The yield of the target product is rather high (up to 85–90%), but the use of an excess of toxic V-containing compounds does not allow to consider this method as an environmentally benign alternative to chromium oxide-based stoichiometric oxidation of MN. The oxidation of MNL with excess [bis(trifluoroacetoxy)]iodobenzene was published to give 80% MNQ yield [30]. Thus the development of MNL oxidation process using an atom efficient, clean and cheap oxidant still remains a challenge.

Hydrothermally stable mesoporous titanium-silicates [31–34], supported metal phthalocyanines [35–38] and gold nanoparticles [39–43] are among the most promising heterogeneous catalysts for liquid-phase selective oxidation of a wide variety of organic compounds. Importantly, all three types of catalytic materials do not contain poisonous components, which is essential for vitamin production. Here we report the main regularities and characteristics of three recently found methods of MNQ production based on the oxidation of MNL: (1) with aqueous H_2O_2 over hydrothermally stable mesoporous titanium-silicate Ti-MMM-2, (2) with *tert*-butyl hydroperoxide (TBHP) over iron phthalocyanine supported on SiO_2 ($FePcS/SiO_2$) and (3) with molecular oxygen over supported gold catalysts. Unexpectedly promising results of a non-catalytic MNL oxidation with molecular oxygen are also reported and compared with the results of the other methods.

2. Experimental

2.1. Materials

2-Methyl-1-naphthol (MNL, 98%) and 2-methyl-1,4-naphthoquinone (MNQ) were purchased from Aldrich and used as received. The concentration of hydrogen peroxide (27–30%) was determined iodometrically prior to use. TBHP (Aldrich) was used as 70% aqueous solution. Gold of 99.9999 purity in sponge, D-glucose monohydrate (99% pure), $NaBH_4$ of purity >96% from Fluka and carbon supports, X40S from CAMEL (C-1, specific area S 1100 $m^2\,g^{-1}$, pore volume V 0.37 ml g^{-1}) and acetylene black from CPChem (C-2, S 75 $m^2\,g^{-1}$) were used. All the other reactants were obtained commercially and used without further purification.



Scheme 2. By-products in 2-MN oxidation.

2.2. Catalysts

Ti-MMM-2 (1.78 wt.% Ti) was prepared under moderately acidic conditions using $Na_2Si_2O_5$ and $Ti(SO_4)_2{\cdot}H_2SO_4$ as silica and titanium sources, respectively, and cetyltrimethyl ammonium bromide as template as it was described recently [31]. The surfactant was removed from as-synthesized form by calcination in air at 560 °C for 5 h. The freshly calcined sample was characterized by elemental analysis, N_2 adsorption measurements and DRS-UV [31,34]. Iron tetrasulfophthalocyanine (FePcS) was prepared according to the modified method of Weber and Busch [44,45]. The heterogeneous catalyst FePcS/SiO_2 was prepared by covalent drafting of $FePc(SO_2Cl)_4$ onto amino-modified SiO_2 as previously described [13] and characterized by chemical analysis, surface area determination and the diffuse reflectance UV–vis spectroscopy that evidence the complex grafting. The complex contents were determined by metal analysis using an inductively coupled plasma-mass spectroscopy method to be 35–40 μmol/g. Supported gold catalysts were prepared by immobilization of preformed gold sols [39,40]. A solution containing D-glucose monohydrate ($0.35\ \text{mol L}^{-1}$) and $HAuCl_4$ ($1.25 \times 10^{-4}\ \text{mol L}^{-1}$) was treated under vigorous stirring with a freshly prepared solution of $NaBH_4$ ($NaBH_4$:Au = 5 mol mol^{-1}) to produce a brown-tea colloidal dispersion. The colloidal sol was immobilized on carbon by adding the support material to the solution under stirring to produce the theoretical amounts of 1% and 2.5% of Au. After 2 h, the slurry was filtered and washed with hot water until the filtrate was chloride free. The complete adsorption of gold was confirmed by ICP analysis of the residue metal in the mother liquid, using a Jobyn Yvon JY24 instrument. The Au/TiO_2 (1.5 wt.% Au) was a gold reference catalyst supplied by the "World Gold Council" (diameter of gold particles measured by TEM observation was 3.7 nm).

2.3. Catalytic experiments

Catalytic oxidations with H_2O_2 and TBHP were performed under vigorous stirring in thermostated glass vessels in the range of 20–80 °C. Oxidations with molecular oxygen (1–3 atm) were carried out in special Pyrex glass reactors under vigorous stirring at 20–80 °C. The oxidation products were identified by GC–MS and ^{1}H NMR, MNL and MNQ were quantified by GC using biphenyl as internal standard. The crude product was separated by thin layer chromatography on a silica gel plate using toluene and toluene/diethyl ether (30:1) as eluents. After the reactions, Ti-MMM-2 catalysts were filtered off, washed with methanol and acetonitrile, dried in air at 100 °C for 5 h and then re-used.

2.4. Instrumentation

GC analyses were performed using gas chromatographs "Crystall 2000" and "Agilent 6890" equipped with a flame ionisation detector and a catharometer, respectively, and quartz capillary columns filled with Carbowax 20 M (25 m × 0.3 mm) and Supelcowax 10 Fused Silica Capillary Column (15 m × 0.32 mm), respectively. GC–MS analyses of organic products were conducted using a HP 5973/6890 system (electron impact ionization at 70 eV, He carrier gas, 30 m × 0.25 mm crosslinked 5% PHME siloxane (0.25 μm coating) capillary column, HP-5MS) or a VG-7070 instrument. ^{1}H NMR spectra were recorded on an MSL-400 Bruker spectrometer. DRS-UV measurements were performed on a Shimadsu UV-VIS 2501PC spectrophotometer. Nitrogen adsorption isotherms at 77 K were measured using a Quantachrome Autosorb-6BKr instrument. XRD (Rigaku D III-MAX horizontal-scan powder diffractometer with Cu Kα radiation) analysis was performed to determine the size of the gold crystallites (mean particle size was 3.6 nm) according to the Scherrer equation.

3. Results and discussion

Recently, we reported the optimization of the Ti-MMM-2 catalyst and reaction conditions for MNL oxidation to MNQ [34]. The reaction temperature, the solvent nature and the catalyst (Ti)/substrate molar ratio had a pronounced effect on the menadione yield (Fig. 1). MeCN was the solvent of choice. The selectivity to MNQ increases with increasing temperature and catalyst amount. One of the main parameters that strongly affect MNQ selectivity is concentration of MNL. The selectivity significantly increases with decreasing naphthol

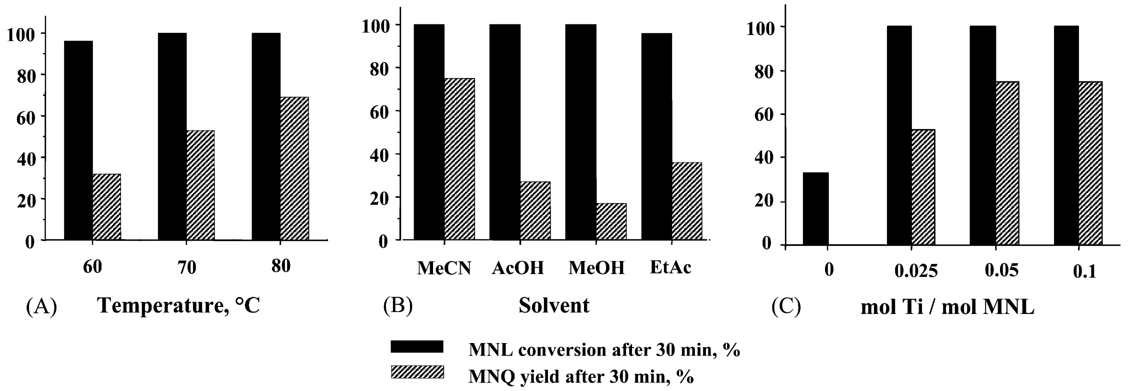


Fig. 1. The effect of temperature (A), solvent (B) and catalyst amount (C) on the MNL oxidation with H_2O_2 over Ti-MMM-2 (1.78 wt.% Ti). Reaction conditions: MNL, 0.025 M; H_2O_2, 0.125 M; cat. 5 mol% (3.8 mg) (A) and (B), 80 °C (B) and (C), MeCN 1 mL (A) and (C), 30 min.

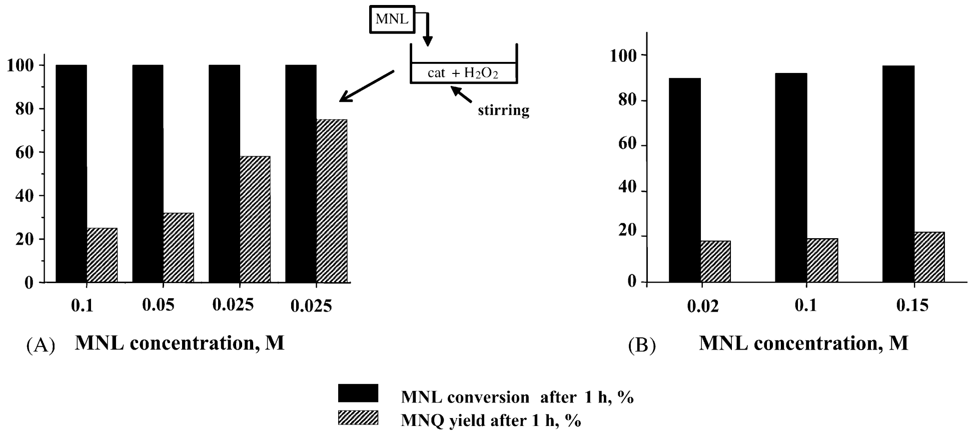


Fig. 2. The effect of MNL concentration on its oxidation with H_2O_2 over Ti-MMM-2 (A) and with TBHP over FePcS/SiO_2 (0.2 wt.% Fe) (B). Reaction conditions: (A) Ti-MMM-2, Ti/MNL = 1/20; MNL/H_2O_2 = 1/5; MeCN, 1 mL; 80 °C; 30 min; (B) FePcS/SiO_2, Fe/MNL = 1/100; MNL/TBHP = 1/3; MeCN, 1 mL; 40 °C; 2 h.

concentration (Fig. 2). Stepwise addition of the concentrated solution of MNL to the reaction mixture also allows to increase the product yield. Oppositely, stepwise addition of H_2O_2 leads to decreasing selectivity. Note that such a drastic dependence of the selectivity to monoquinone is typical for a few known catalytic oxidations of substituted phenols (naphthols) and is due to one-electron oxidation mechanism, involving the formation of aryloxyl radicals, the coupling of which yields dimeric by-products [46,47]. Indeed, 4,4-di(2-methyl-1-naphthol) and 4,4-di(2-methylnaphthoquinone) were found as the main by-products in MNL oxidation over Ti-MMM-2. Previously, we have demonstrated that Ti-MMM-2 behaves as a true heterogeneous catalyst, does not suffer from titanium leaching and can be recycled [31,32]. Fig. 3 shows that the catalytic activity and selectivity of Ti-MMM-2 in MNL oxidation with H_2O_2 remains unchanged during several catalytic cycles (Fig. 3).

The advantages of the Ti-MMM-2/H_2O_2 system are the use of clean and cheap oxidant, true heterogeneous, easily recyclable catalyst, no Cl-containing solvents and reagents and, as a result, high purity of the resulting product. The *E*-factor was estimated to be about 0.3 (compare with $E = 18$ in the CrO_3-based method). All this allows one to view the MNL oxidation with H_2O_2 over Ti-MMM-2 as an environmentally benign procedure. The main drawback, however, is the dramatic decrease of the selectivity with increasing substrate concentration leading to a low volume yield of the target product.

The MNL oxidation with TBHP over FePcS/SiO_2 follows trends similar to those observed for the Ti-MMM-2/H_2O_2 system with increasing temperature (Fig. 4A) and catalyst amount (Fig. 4B) but the optimal catalyst/substrate ratio is lower for FePcS/SiO_2/TBHP than for Ti-MMM-2/H_2O_2 (compare Figs. 1C and 4B). The best selectivity to MNQ was achieved with 0.5–0.8 mol% of the FePcS/SiO_2. In sharp contrast to the titanium/H_2O_2-based oxidation, no strong dependence of the MNQ selectivity on MNL concentration was found in the FePcS/TBHP system (Fig. 2B), suggesting a different mechanism of MNL oxidation in this system. Indeed, the typical one-electron oxidation products (dimeric dinaphthoquinone and dinaphthol) were not detected with the FePcS/SiO_2 catalyst using TLC and NMR. Furthermore, 2,3-epoxy-2-methyl-1,4-naphthoquinone was identified by GC–MS indicating an oxygen transfer mechanism. The recycling experiments

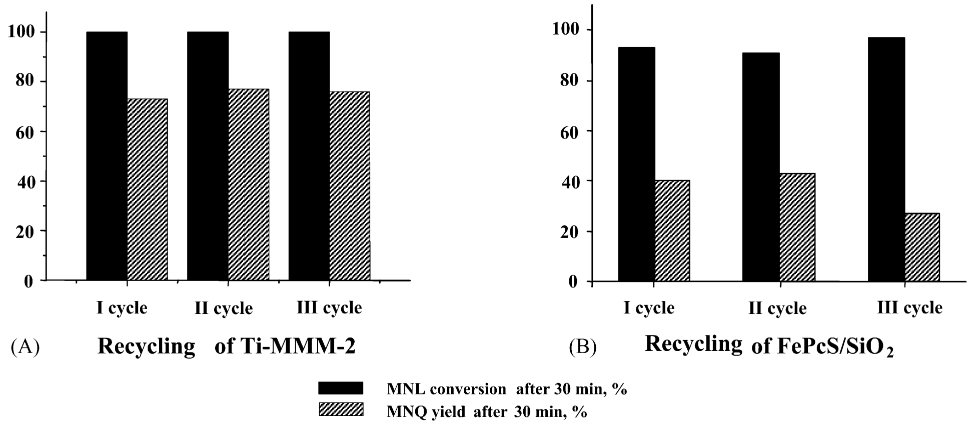


Fig. 3. Ti-MMM-2 (A) and FePcS/SiO_2 (B) recycling in MNL oxidation. Reaction conditions: (A) MNL, 0.025 M; H_2O_2, 0.125 M; Ti-MMM-2, 5 mol% (3.8 mg); MeCN, 1 mL; 80 °C; 30 min, MNL solution in 250 μL of MeCN was added to the reaction mixture by portions 50 μL/2 min; (B) MNL, 0.025 M; TBHP, 0.125 M; FePcS/SiO_2, 1 mol% (6.4 mg); MeCN, 1 mL; 80 °C; 30 min, MNL solution in 250 μL of MeCN was added to the reaction mixture by portions 50 μL/2 min.

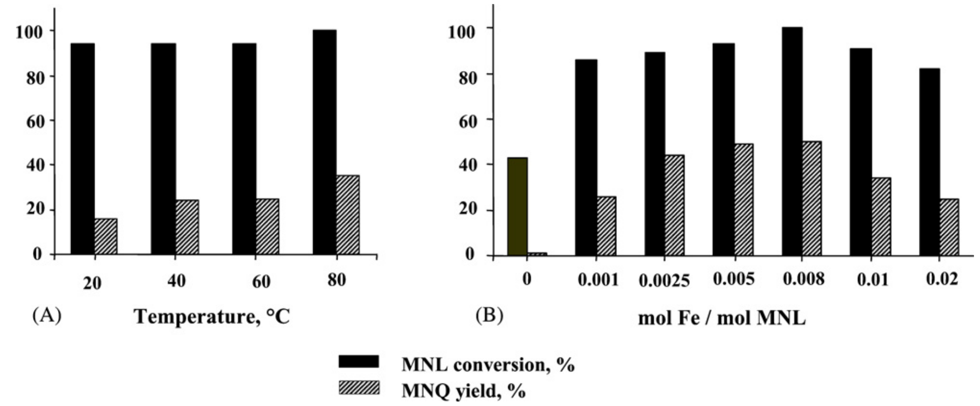


Fig. 4. The effect of temperature (A) and catalyst amount (B) on the MNL oxidation with TBHP over FePcS/SiO_2. Reaction conditions: MNL, 0.1 M; TBHP, 0.3 M; MeCN, 1 mL; (A) FePcS/SiO_2, 1 mol% (25.7 mg); 1 h and (B) 30 min; 40 °C.

showed that FePcS/SiO_2 kept the same catalytic activity without significant change of selectivity of the MNL oxidation during at least two catalytic cycles (Fig. 3B).

MNL oxidation with molecular oxygen was also studied in the presence of gold nanoparticles supported on three different inorganic supports, including two types of activated carbon and anatase. At atmospheric pressure, the reaction is rather slow, while at 3 atm of O_2 moderate yields of MNQ are attained after 6 h (Table 2). The nature of support affects both the activity and selectivity. Thus, the hydrophilic catalyst Au/C-1, containing 34 wt.% of water, is less active and selective compared to the hydrophobic Au/C-1. The nature of solvent plays a dramatic role (Fig. 5A). The most promising results were obtained in toluene. In CCl_4, the reaction is fast but selectivity is rather poor. Like in the case of Ti-MMM-2/H_2O_2 system, the MNQ selectivity increases with lowering MNL concentration (Fig. 6A). It also slightly increases with rising oxygen pressure (Fig. 6B) and temperature.

While running blank experiments, we have revealed that carbon support (without Au) retards the MNL oxidation with O_2 (Table 2). In fact, the reaction is faster in the absence of any additives (true blank experiment) and produces MNQ with even better selectivity than in the presence of the supported gold catalysts, indicating that the latter most likely enhance overoxidation processes along with MNL oxidation to MNQ.

Table 2
MNL oxidation with O_2 in presence of supported Au-catalysts

Catalyst[a]	MNL conversion (%)	Menadione yield[b] (%)
2.5% Au/C-1	86	56
1% Au/C-1[c]	79	45
1% Au/C-2	94	49
C-2	23	49
1.5% Au/TiO_2	82	57

Reaction conditions: P(O_2) 3 atm, [MNL] = 0.1 M, catalyst 3–7.5 mg (MNL(mol)/Au(mol) = 250), toluene 3.5 mL, 80 °C, 6 h.

[a] Catalyst specification see in Section 2.

[b] Based on converted substrate.

[c] Hydrophylic catalyst containing 34 wt.% of H_2O.

Again, the solvent nature dramatically affects the reaction, and a proper choice of solvent is a key point for both activity and selectivity (Fig. 5B). In non-polar solvents, including toluene, carbon tetrachloride and cyclohexane, a very good level of selectivity was achieved (up to 85–90%) [48]. The selectivity does not decrease with the substrate conversion indicating that the quinone product is stable to overoxidation, which has been confirmed in independent experiments.

Highly important is that, in sharp contrast to the Ti/H_2O_2, Au/O_2 and V-HPA [27,29] catalytic systems, the selectivity of the non-catalytic MNL oxidation does not suffer from rising

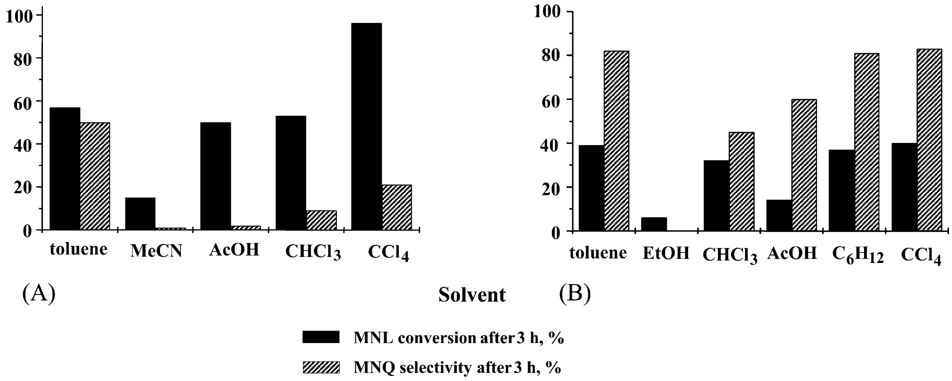


Fig. 5. The effect of solvent on the MNL oxidation over supported gold catalysts (2.5 wt.% Au) (A) and without catalyst (B). Reaction conditions: MNL, 0.1 M; O_2, 3 atm; solvent, 3.5 mL; 80 °C; 3 h; (A) Au/C-1 0.1 mol% (3 mg).

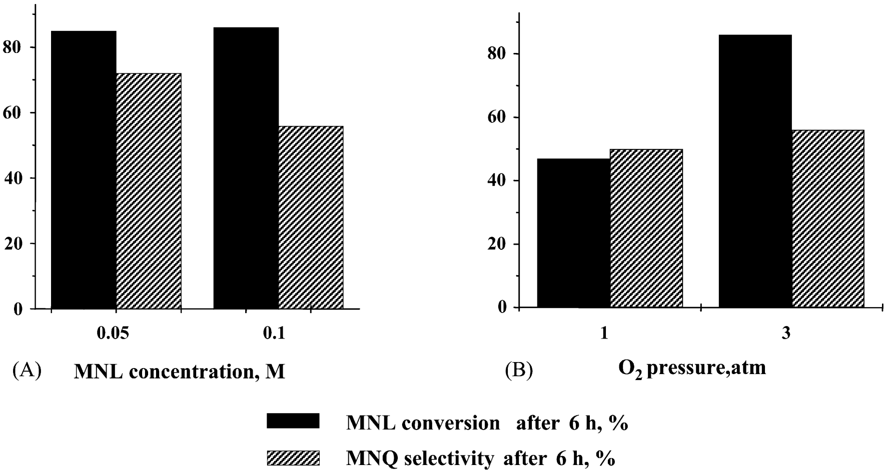


Fig. 6. The effect of MNL concentration (A) and $P(O_2)$ (B) on the MNL oxidation with O_2 over Au/C-1. Reaction conditions: Au/C-1 0.1 mol% (3 mg), toluene 3.5 mL, 80 °C, 6 h, (A) O_2 3 atm and (B) MNL 0.1 M.

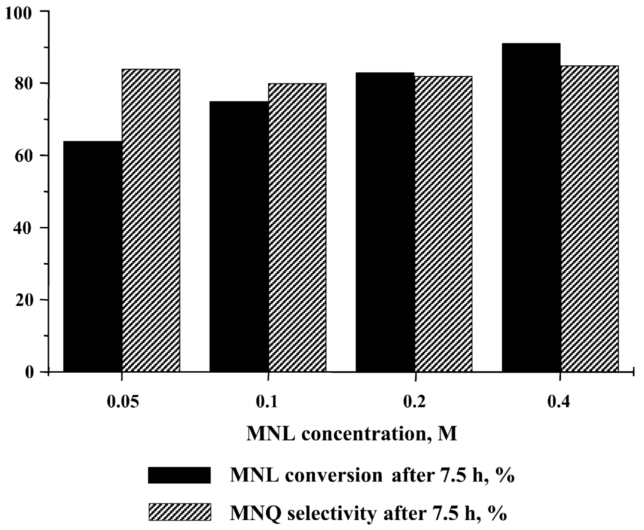


Fig. 7. The effect of substrate concentration on MNL oxidation with molecular oxygen. Reaction conditions: O_2, 3 atm; toluene, 3.5 mL; 80 °C; 7.5 h.

MNL concentration (Fig. 7). Indeed, the dimeric products that arise from coupling of aryloxyl radicals were not found in this reaction and MNQ yield was as high as 80–90% depending on the solvent. In principle, the reaction can be carried out even in melting substrate. That means that high volume yield of MNQ can be obtained, which was not possible in the other known methods.

Another interesting feature of the non-catalytic reaction is that the selectivity to MNQ does not fall significantly with decreasing temperature, while the latter is typical for the catalytic phenol (naphthol) oxidations [27,34,46]. The non-catalytic MNL oxidation with O_2 proceeds selectively even at room temperature (Table 3). However, the oxygen pressure is important: at 1 atm of air, no MNL conversion was found after 66 h.

The comparison of the most important characteristics of the five different approaches to MNQ, including the CrO_3 [3], V-HPA/O_2 [28], Ti-MMM-2/H_2O_2, FePcS/SiO_2/TBHP and "O_2" methods is given in Fig. 8. Space time yield (STY) is more or less similar for all the procedures, because low MNL concentration is compensated by a fast reaction rate in the case of Ti-MMM-2/H_2O_2 and vice versa for the "O_2" method. However, the volume yield in the non-catalytic MNL oxidation

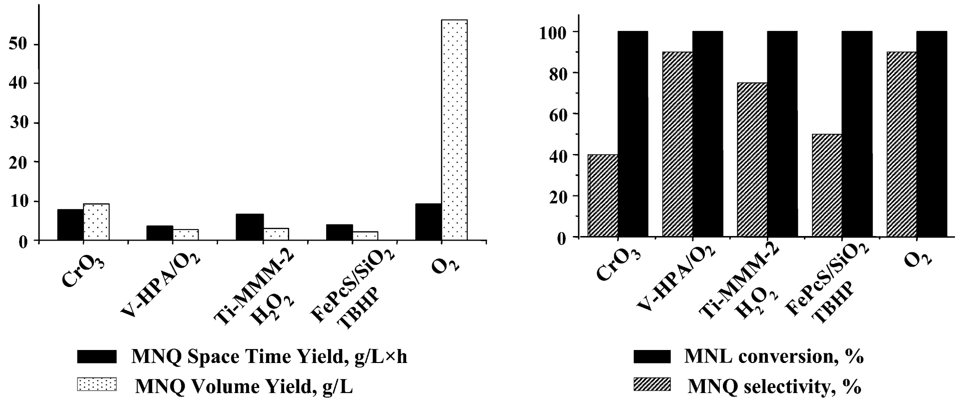


Fig. 8. Menadione production: comparison of different methods. The space time yield and volume yield of V-HPA/O_2 and CrO_3-based systems were calculated from the data reported in Refs. [28,3], respectively.

Table 3
MNL oxidation with O_2 (3 atm) at room temperature

Solvent	[MNL] (M)	Time (h)	MNL conversion (%)	MNQ selectivity (%)
Toluene	0.4	162	87	80
CCl_4	0.1	72	37	84
		171	80	81

with O_2 is much higher compared to the other methods (more than 60 g/L, Fig. 8A). The highest selectivity to MNQ is accomplished in the "O_2" and V-HPA/O_2 methods (Fig. 8B). The advantages of the "O_2" method are evident. These are the simplicity of operation, low cost, high volume yield and low energy consumption (it is possible to operate even at room temperature).

4. Conclusions

MNL can be easily oxidized to MNQ with aqueous H_2O_2 over true heterogeneous and recyclable Ti-MMM-2 catalyst with good selectivity but low volume yield. FePcS/SiO_2/TBHP and Au/C/O_2 catalytic systems provide MNQ with moderate selectivity and volume yield. In a proper chosen solvent, MNL can be selectively oxidized to MNQ with molecular oxygen without any catalyst producing the target Vitamin K_3 with both high selectivity and high volume yield.

Acknowledgments

We thank C. Guidi for GC–MS measurements and N. Dimitratos for help. O.A.K acknowledges the Cariplo-Foundation-Centro Volta for a full professor fellowship and O.V.Z acknowledges French Embassy in Moscow for a doctoral fellowship. The research was partially supported by Russian Foundation for Basic Research (grant RFBR-CNRS 05-03-34760) and by CNRS (Institut de Recherches sur la Catalyse and Boreskov Institute of Catalysis Associated European Laboratory).

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