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(54) Title: REDOX PROCESS PARTICULARLY FOR THE PRODUCTION OF MENADIONE AND USE OF POLYOXOMETALATES

(57) Abstract: The present invention relates to a redox process particularly but not exclusively for producing menadione, which uses Keggin-type heteropolycompounds as oxidizing agents. These compounds are polyoxometalates containing phosphorus, molybdenum, tungsten, vanadium and oxygen, which by virtue of their chemical properties can be used as oxidizers in many redox processes. This redox process can be applied advantageously to products obtained by virtue of a new process of alkylation of 1-naphthol with alcohols. In a particularly preferred case of combination between the alkylation process and the redox process, the 1-naphthol is alkylated with methanol to 2-methyl-1-naphthol, which is then oxidized to menadione.



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REDOX PROCESS PARTICULARLY FOR THE PRODUCTION OF MENADIONE AND USE OF POLYOXOMETALATES

Technical field

The present invention relates to a redox process particularly but not exclusively for the production of menadione, to the use of heteropolycompounds containing vanadium as oxidizing agents, and to a synthetic strategy of alkylation and subsequent oxidoreduction of organic substrates that comprises the coupling of a process for alkylation of 1-naphthol with the subsequent oxidation of the alkylated products.

Background art

Menadione (2-methyl-1,4-naphthoquinone or vitamin K₃) is the first and most important synthetic analog of natural vitamin K and is the initial substrate for synthesis of all other vitamins of the K family in use and currently commercially available.

Industrial preparation of menadione is currently performed by various methods, the most widely used of which is certainly oxidation of 2-methylnaphthalene with salts of Cr^{VI}.

The chromium reduced to trivalent chromium during the oxidation process is then usually treated for suitable disposal. Yield and selectivity to menadione are rather low, typically around 50%, the remainder goes partly to the menadione isomer 6-methyl-1,4-naphthoquinone and partly to other products. In any case, the environmental and safety problems linked to the disposal of wastewater containing the metal ion and to the use of Cr^{VI}, which is known to be a compound with high toxicity characteristics, has stimulated the search for alternative synthesis methods that do not use chromium as stoichiometric oxidizer.

Among the proposed alternatives, mention can be made of oxidation with cerium methanesulfonate and subsequent electrolytic reoxidation of the reduced cerium (Kreh et al., J. Appl. Electrochem. 20, (1990) 201), and of

oxidation with H_2O_2 and acetic acid in the presence of a Pd catalyst (Yamaguchi, Inoue, Enomoto—Bull. Soc. Chim. Jap., 59 (1986) 2881).

In this case also, yield and selectivity to menadione are not very high and moreover the difficult and high cost of the two processes do not make them competitive with respect to other known technologies that are currently used.

One technique introduced by Matveev et al. (J. Molec. Catal., A. Chemical 114 (1996) 151) is based on oxidation of 2-methyl-1-naphthol with Keggin-type heteropolycompounds.

So-called heteropolycompounds (or polyoxometalates) are based on the structure of Keggin-type heteropolyanions, which have the general composition $\text{XM}_{12}\text{O}_{40}^{n-}$ in which X is the central atom (usually Si^{4+} or P^{5+}), and M is a metal ion, typically Mo^{6+} and/or W^{6+} , which can be substituted partially by other metal ions (example V^{5+} , Co^{2+} , Zn^{2+} ...). These polyoxometalates are oxidizers and/or catalysts, which are used in reactions of organic compounds of various kinds, although they are not all regenerable oxidizers.

The use of these inorganic compounds for this reaction has been described in several publications (K.I. Matveev, V.F. Odyakov and E.G. Zhizhina, J. Molec. Catal., A. Chemical 114 (1996) 151; K.I. Matveev, E.G. Zhizhina and V.F. Odyakov, React. Kinet. Catal. Lett., 5581) (1995) 47; Russian patent 2061669 dated 1996 and Russian patent no. 2142935 dated 1997), and is part of a technology known as "Vikasib" for the production of some vitamins of the K family starting from 1-naphthol. These publications describe the conditions for synthesis of menadione, such as for example the reaction temperature, the solvent, and the ratio between the substrate to be oxidized and the oxidizing agent (which is generally less than 1).

In the patents cited above, attention is focused on the first stage of the redox process, i.e., on the synthesis reaction of 2-methyl-1,4-naphthoquinone. The stage for reoxidation of the reduced compound, which

is equally crucial for the low cost of the overall redox process, is instead mentioned only briefly.

Russian patent 2142935 dated 1997, which uses a compound having the formula $H_6PMo_9V_3O_{40}$, refers to a process for reoxidation of the reduced
5 inorganic compound, in which during the synthesis step a fraction of an aqueous solution of hydrogen peroxide is added in an amount that is equivalent, in terms of number of moles, to the moles of heteropolycompound present in the reaction environment. Moreover, in order to reduce the contribution of parasitic reactions of condensation of
10 menadione with 2-methyl-1-naphthol, during the reaction the organic phase that contains the reaction products is separated a few times from the system. After the final separation of the two phases, the aqueous solution is in any case treated further with molecular oxygen at 100 °C.

The goals of such a complex reoxidation procedure are to keep the
15 average state of oxidation of the heteropolycompound as high as possible during synthesis (since it is claimed that this leads to higher selectivities and yields) and to reduce considerably the times required for reoxidation of the reduced compound, which is performed entirely separately.

None of the cited documents, therefore, teaches that the heteropolyacid
20 can be regenerated easily in bland conditions (such as with oxygen at atmospheric pressure) and can be recycled continuously in the oxidation process while keeping yield and selectivity unchanged.

Therefore, the possibility to identify operating conditions that allow reoxidation of the reduced inorganic compound in a short time with a simple
25 and reliable procedure by using only molecular oxygen in relatively bland conditions would be a significant improvement of the redox process per se and of the overall menadione synthesis process.

It is also necessary to stress that in any case the scientific literature in this regard has not yet achieved the optimum situation, which provides for

similar rate (in similar conditions) for the organic substrate oxidation step and the oxidizing agent reoxidation step or even a higher rate of the latter, so that the synthesis stage is the kinetically decisive one of the entire process.

Accordingly, the aim of the present invention is to provide a redox process for oxidation of phenols, naphthols, and optionally substituted derivatives thereof, particularly for the production of menadione, that ensures high yields and selectivities with respect to the products, in which the stages for substrate reduction and restoration of activity of the oxidizing agent have mutually comparable rates, provides for easy and rapid restoration of the oxidizing activity of the inorganic reagent, and uses an oxidizing agent with low toxicity, high solubility in at least one (commonly used) solvent, and an oxidation potential of the [oxidized agent/reduced agent] pair that is lower than the potential of the [organic reagent/organic product] pair but allows reoxidation in bland conditions.

15 Disclosure of the Invention

This aim and other objects are achieved, according to the invention, by means of a redox process for preparing an oxidized organic compound, comprising the steps of:

a1) reacting an oxidizable organic compound chosen among phenols, naphthols and optionally substituted derivatives thereof, with one or more polyoxometalate compounds having the general formula



where

Me is a metal ion chosen from the group that comprises Na^+ , K^+ , Li^+ , Cs^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Al^{3+} , Fe^{3+} , La^{3+} , Ce^{3+} , Cr^{3+} , or a combination thereof;

a is the valence of Me,

m is comprised between 0 and 7, depending on a and n;

n is comprised between 1 and 4,

p is comprised between 0 and 6,

said polyoxometalate compounds being characterized in that the average oxidation number calculated on the total vanadium atoms is greater than 4,

b1) recovering the organic product of the reaction of a1),

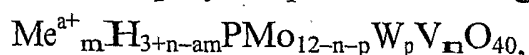
5 c1) restoring the average oxidation state of the vanadium in said polyoxometalate compounds so that it is comprised between 4 and 4.95, making said polyoxometalate compounds react with a compound that has a lower oxidation potential than said polyoxometalate compounds,

10 d1) repeating the three preceding steps one or more times, using the product of c1) as polyoxometalate compound in the subsequent steps a1).

Ways of carrying out the Invention

Further advantages and characteristics of the invention will become better apparent from the description of a preferred but not exclusive embodiment of the claimed process.

15 The inorganic compound that constitutes the organic substrate oxidizing agent is constituted by a Keggin-type heteropolycompound in aqueous solution, and its use as an oxidizing agent is another aspect of the invention; as mentioned above, the heteropolycompound has the general formula



20 where

Me is one or more metal ions, for example Na^+ , K^+ , Li^+ , Cs^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Al^{3+} , Fe^{3+} , La^{3+} , Ce^{3+} , Cr^{3+} , preferably Na^+ and Fe^{3+} ;

a is the valence of Me,

25 m is comprised between 0 and 7, preferably equal to 0, depending on a and n,

n is comprised between 1 and 4, preferably equal to 2,

p is comprised between 0 and 6, preferably equal to 0.

According to the invention, the polyoxometalate thus defined can be used as oxidizing agent either by using a mixture of the polyoxometalates that

match the definition given or preferably by using a single one.

By way of example, the preferred embodiments presented herein describe in particular the reactivity of a heteropolycompound having the composition $H_5PMo_{10}V_2O_{40}$, but the principle on which the present invention is based has a fully general connotation and therefore can be extended to any heteropolycompound whose structure can be traced back to the Keggin type, containing at least one vanadium atom by formula, usable for stoichiometric oxidation of phenol or naphthol and derivatives thereof.

The following are examples of oxidation reactions of particular interest, in which the particular redox process configuration according to the present invention can be applied:

2,3,6-trimethylphenol to 2,3,5-trimethyl-1,4-benzoquinone,
2,3,4,6-tetramethylphenol to 2,3,5-trimethyl-1,4-benzoquinone,
2,6-dialkylphenols to diphenoquinones (oxidative dimerization).

However, as described more clearly hereafter, the redox process according to the invention is applied advantageously to naphthols and to optionally substituted derivatives thereof and even more preferably to 2-methyl-1-naphthol, so as to lead to menadione.

Unexpectedly, the present invention can advantageously entail similar rates for the synthesis step and for the reoxidation step.

This last aspect is therefore one of the most important advantages of the present invention with respect to the background art, since it allows to use two reactors of similar capacities for the two stages, or even the same reactor for both stages, with a significant saving on investment costs. Moreover, the dimensions of the equipment and of the reactor can be calibrated, in this manner, according to the actual productivity requirements of the product of interest.

Conversely, a reoxidation rate much slower than the synthesis rate (at least in the reaction conditions used up to now) led to considerably longer

filling times for the second stage with respect to the synthesis stage and therefore to a much larger volume for the reoxidation reaction, with a considerable cost increase. As an alternative, it became necessary to mitigate the reaction conditions for the synthesis stage in order to adapt the productivity of the first stage to the rate of the second stage, but limiting the productivity of the redox process.

Furthermore, by performing the reoxidation step in bland conditions, regardless of the polyoxometalate catalyst chosen, the time used to restore the average oxidation number of the vanadium according to the present invention is in any case comprised between a minimum of 0.5 hours and a maximum of 15 hours. These values are very different from the values (150 hours) of the teachings available in the literature for total restoration in bland conditions of the oxidation state of the vanadium, which up to now was thought to be a binding constraint for restoring the oxidizing activity of the polyoxometalate. These values are also conceptually far removed from the other known method of fully restoring the oxidation state of the vanadium, i.e., to resort to conditions that are anything but bland in the hope of shortening the times of the restoration procedure.

In detail, the process according to the present invention, when applied in a preferred manner to 2-methyl-1-naphthol in order to obtain 2-methyl-1,4-naphthoquinone, comprises the following stages.

The first step entails a first reaction of synthesis of the 2-methyl-1,4-naphthoquinone by oxidation of 2-methyl-1-naphthol on the part of one or more Keggin-type heteropolycompounds containing P, Mo and V, plus optionally other ions of transition metals, as known from the literature; the general composition of said heteropolycompounds is $\text{Me}^{a+}_m\text{H}_{3-n-am}\text{PMo}_{12-n-p}\text{W}_p\text{V}_n\text{O}_{40}$, where Me is a metal ion selected from the group that comprises Na^+ , K^+ , Li^+ , Cs^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Al^{3+} , Fe^{3+} , La^{3+} , Ce^{3+} , Cr^{3+} , or a combination thereof; a is the valence of Me, m is comprised

between 0 and 7 depending on a and n; n is comprised between 1 and 4, and p is comprised between 0 and 6.

The synthesis reaction can be performed in a two-phase system of aqueous solution/organic solvent, in which the oxidizing agent (the heteropolycompound) is present in one of the two phases, usually the aqueous one, while the organic substrate and the reaction product, together with any byproducts, remain predominantly dissolved in the second phase, usually the organic one, or vice versa. Contact between the two phases is ensured by vigorous mechanical agitation (interrupting the mixing interrupts the reaction).

Regardless of the reagents used (i.e. the oxidizable organic compound and the oxidizing agent), preferably but not exclusively, the reaction is performed at a temperature between 25 ° and 100 °C, preferably at 50 °C, with a concentration of 2-methyl-1-naphthol at most equal to 0.1M, preferably 0.06M in a solvent such as hexane or in another suitable solvent and of heteropolycompound comprised between 0.02 and 0.5 M, preferably equal to 0.4M in a solvent such as water. The addition of the reagent to the solution that contains the catalyst preferably occurs in a time interval comprised between 0.5 and 8 hours (typically 2 hours).

According to this method, a practically complete reagent conversion is achieved together with a selectivity, which coincides with the yield, comprised between 75% and 85%.

Regardless of the specific polyoxometalate used, as regards the degree of vanadium reduction (defined with the symbol α_V), some preliminary remarks must be made.

The degree of reduction of vanadium indicate the percentage ratio between vanadium^{IV} (reduced) and total vanadium (oxidized vanadium^V + reduced vanadium^{IV}) in the heteropolycompound, and is evaluated both before oxidation of the methyl-naphthol (therefore in the fully efficient

oxidizer) and after, i.e., before reoxidation of said heteropolycompound.

Numerous experimental tests have been conducted in which the type of oxidizer and its ratio with respect to the organic substrate has been varied, highlighting the following aspects.

5 In the case of a catalyst like $H_5PMo_{10}V_2O_{40}$, used in a 4:1 molar ratio with respect to the substrate, one obtains a α_V equal to approximately 50% after a first synthetic cycle, for a total conversion of the substrate. This is in accordance with the stoichiometry of the reaction, since four vanadium atoms are needed for each naphthol molecule.

10 In the same case, for any initial degree of reduction (α_V 95%, 70%, 50%), one obtains after reoxidation an α_V equal to 25%-27%, a value at which the rate of this reaction at 100 °C and at atmospheric pressure becomes very low or negligible.

15 In the case of a catalyst such as $H_4PMo_{11}V_1O_{40}$, the α_V after the synthesis step is close to 90%, while after reoxidation it is equal to 65%-80%. This means that on the one hand, the effectiveness of the heteropolycompound depends on the presence of at least one vanadium atom, but on the other hand the value of α_V can vary among heteropolycompounds, making a catalyst less suitable for a cyclic process.

20 Finally, the rate of the reoxidation process seems to be a function of the concentration of the heteropolycompound in the solution rather than of the type of heteropolycompound.

It has also been verified experimentally that a catalyst (for example $H_5PMo_{10}V_2O_{40}$) in which the degree of reoxidation α_V is less than 100% (for
25 example α_V equal to 25-30%) does not exhaust its oxidizing power even after a few synthetic cycles.

One may surmise that probably the solution does not contain a specific species of heteropolycompound but rather a distribution of compounds having the general formula $H_{3+n}PMo_{12-n}V_nO_{40}$ (with $n \geq 1$) and in which said

distribution is governed by thermodynamics or by the type of initial heteropolycompound (therefore by the ratio between molybdenum and vanadium).

To conclude, it is possible to set up a cyclic redox process that uses the catalyst indefinitely without having to adopt drastic (and long-lasting) conditions for reoxidation in order to restore its initial α_V , while unexpectedly maintaining yield and selectivity values that are fully acceptable and similar to those present in the literature.

Finally, as regards the degree of reduction after the first synthetic cycle, it has been found experimentally that the α_V approaches the value that can be obtained by means of the following formula:

$$\text{Red. \%} : 4 \times (\text{MN/HPC}) \times (1/n) \times 100$$

where MN/HPC is the molar ratio between the 2-methyl-1-naphthol and the heteropolycompound and where n is the number of atoms of V per Keggin unit.

This relation holds only if the value $[4 \times (\text{MN/HPC}) \times (1/n)] \leq 1$; otherwise the degree of reduction is 100%.

To support this statement, the following table lists a few experimental values obtained by varying the heteropolycompound:

HETEROPOLYCOMPOUND	YIELD	MN/HPC	DEGREE OF REDUCTION
$\text{H}_4\text{PMo}_{11}\text{V}_1\text{O}_{40}$	Between 75% and 85%	1 / 4	Between 80% and 100%
$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	Between 75% and 85%	1 / 4	Between 40% and 60%
$\text{H}_6\text{PMo}_9\text{V}_3\text{O}_{40}$	Between 75% and 85%	1 / 4	Between 20% and 40%

A second step entails the partial reoxidation of the heteropolycompound reduced during the first step.

This stage is one of the most interesting aspects of the present invention and one of the main innovation with respect to what is known in the literature.

In particular, the reoxidation stage can be performed with oxygen at atmospheric pressure and at a temperature between 80 and 110 °C, preferably 100 °C, until the average oxidation number of the total vanadium present is restored to a value comprised between 4 and 4.95, preferably between 4.60 and 4.90.

Reoxidation is preferably performed by bubbling the oxygen through the solution containing the heteropolycompound that has undergone reduction during the preceding step. As an alternative, air can be used instead of oxygen, although this entails slowing the rate of reoxidation.

Advantageously, according to the invention this reoxidation treatment is performed in bland conditions and, if for example the compound $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ has been used, for no longer than necessary to reach a degree of reduction of the vanadium approximately equal to 25%-30%.

In the case of $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, had one sought complete restoration of the oxidative state of the vanadium, working with a solution with 0.8% vanadium (weight/weight of solution), one would have had to work at ambient pressure and at 100 °C for over 45 hours, while a value of α_v of 25% is achieved in the same operating conditions in approximately 3 hours. Working instead with a solution of 2.5% vanadium by weight, one would have had to work at ambient pressure and at 100 °C for over 180 hours, while an α_v of 25% is achieved in the same operating conditions in approximately 50 hours.

This aspect entails an evident advantage in terms of process time, despite high yields and selectivities.

After reoxidation in bland conditions, the aqueous solution containing the reoxidized (but in any case still partially reduced) heteropolycompound is ready for a subsequent synthesis stage.

The third step consists of a second cycle of the entire redox reaction.

The partially reoxidized heteropolycompound according to the second

step is reused in the synthesis reaction, in a manner fully similar to the first step.

An advantageous aspect of the present invention is therefore constituted by the fact that the synthesis reaction uses, starting from the second cycle, a heteropolycompound that is recovered from the preceding cycle and contains partially reduced vanadium. This fact is a particularly significant aspect of innovation, since the literature indicates the absolute need to return the average oxidation number of the vanadium to five in order to be able to achieve good catalytic performance.

On the contrary, according to the present invention it has been found surprisingly that when the redox reaction between the heteropolycompound and for example 2-methyl-1-naphthol is performed so as to use a partially reduced heteropolycompound, i.e., in which said average oxidation number is comprised between four and five, one can not only unexpectedly maintain the excellent performance in terms of selectivity and conversion that can be obtained with the fully oxidized heteropolycompound (such as the surprising yields of approximately 80% obtained in the second cycle in example 1 cited hereafter) but can also achieve at the same time considerable advantages in terms of times and costs during the oxidation stages.

To confirm the above (and with the prospect of an "inline" process that cannot be performed with the background art), it is also possible to use a partially pre-reduced heteropolycompound also in step 1 (instead of starting from the fully oxidized compound), without achieving significant variations in catalytic performance. For example, it is possible to pre-reduce the heteropolycompound (for example with hydrated hydrazine) until a vanadium degree of reduction of 25% (again with reference to $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$) is reached.

In this case, step 1 shall provide, like the step 3 described above, a final degree of reduction for the vanadium in the heteropolycompound

approximately equal to 70%-80%. The reoxidation stage (step 2) is then performed as described in the subsequent step.

The fourth step of the process in fact entails the subsequent reoxidation stage, which is performed on the heteropolycompound having a degree of reduction comprised between 70% and 80% (if the conversion of the reagent was completed during step 3) in conditions that are similar to the ones described in step 2, until a degree of reduction for the heteropolycompound equal to 25%-30% is achieved.

The heteropolycompound in aqueous solution is therefore ready to be reused for example in the synthesis of menadione.

The steps after the fourth consist in repeating the third and fourth steps a theoretically indefinite number of times.

In real practice it has been possible to achieve approximately 10 steps, and this is certainly a clear indicator of convenience at the industrial level.

Another interesting aspect of the present invention is constituted by the control of the kinetics of the reoxidation reaction by means of changes to the concentration of the heteropolycompound solution.

In particular, it has been found that if said concentration expressed by weight is less than 2%, it is possible to reoxidize the reduced heteropolycompound to a relative degree of reduction between approximately 25% and 30% in a relatively short time (typically between three and fifteen hours). If instead the concentration is higher than 2%, the rate of said reaction decreases considerably and accordingly the time needed to achieve a comparable degree of reduction increases considerably.

Said concentration can be modified both before step 1 (preparation of the stock solution) and with a process for dilution or evaporation of the solvent prior to step 2 and the subsequent steps.

It has been found that in a preferred and particularly advantageous embodiment, it is possible to proceed so that steps a) and c) have comparable

rates and therefore, together with step b), are performed with a continuous process. In this sense it has in fact been found that steps a) and c) reached comparable rates when the concentration of the compound chosen among phenols, naphthols and derivatives thereof was less than 0.1M, the overall
5 concentration of the polyoxometalates in step a) was between 0.02M and 0.5M, the temperature of step a) was between 25 °C and 100 °C, the temperature of step c) was between 80 °C and 110 °C, and the overall concentration of the polyoxometalates in step c) was less than 2%.

The industrial advantages that derive from performing the entire
10 oxidoreduction step continuously are evident to the person skilled in the art.

Since it is possible to oxidize successfully phenols, naphthols, and optionally substituted derivatives thereof, in the preferred case in which the substrate as mentioned is an optionally replaced naphthol, said substrate is obtained by advantageously associating with the redox process according to
15 the invention a new process for alkylation of 1-naphthol with alcohols.

In particular, the process for alkylation of 1-naphthol that can be advantageously combined with the oxidoreduction process according to the invention comprises the steps of:

a2) placing in contact a mixture that comprises an alcohol and 1-naphthol
20 with a catalyst that contains a mixed oxide of Mg and Fe, said catalyst being prepared from raw materials chosen from salts and oxides of iron containing ferric and ferrous irons and salts and oxides of magnesium,

b2) recovering the alkylated product of step a2) without performing methods for separating said product from byproducts and from the initial
25 unreacted aromatic substrate.

In view of the considerable advantages that are achieved in the alkylation step considered on its own and will be described in detail hereinafter, this single alkylation process also must be considered as a further aspect of the present invention.

The alcohols that can be used in the step for alkylation of 1-naphthol are essentially aliphatic, primary or secondary alcohols, either linear or branched, and with 1 to 6 carbon atoms in the hydrocarbon chain. Preferred examples of alcohols are methanol, ethanol, 2-propanol, 1-propanol, 1-butanol, 2-butanol; other even more preferred examples are methanol, ethanol and 2-propanol, even more preferably methanol.

Iron and magnesium are indispensable components of the active phase of the catalyst for alkylating 1-naphthol.

Useful raw materials containing ionic iron are inorganic substances (salts and oxides) containing ferric and ferrous ions. Preferably, the raw materials containing ionic iron can be iron oxides (ferric and ferrous), maghemite, magnetite, hematite, common inorganic iron salts and mixtures thereof. Even more preferably, said raw materials are iron oxides. Merely by way of example, preferred inorganic iron salts can be iron chlorides and iron nitrates.

Useful raw materials that contain magnesium are inorganic substances (salts and oxides) containing magnesium in ion form. Preferably, magnesium oxide, magnesium chloride and magnesium nitrate are considered.

Preferably, iron and magnesium oxides in any physical form thereof are used. Even more preferably, it is possible to use Fe_2O_3 , hematite, magnetite, maghemite, Fe_3O_4 , FeO and MgO . These oxides can be provided as separate entities, solid solutions or mixed oxides.

Advantageously, said catalyst containing iron and magnesium has an atomic ratio between magnesium and iron (Mg/Fe) comprised in a range between 0.01 and 10, preferably between 0.01 and 5, preferably between 0.01 and 1.5 and even more preferably between 0.05 and 1.5.

The catalyst described for alkylation of 1-naphthol can in any case also contain other optional elements, used for example as dopants. Preferably, said optional elements are other ions of alkaline or alkaline earth metals,

ions of transition or post-transition metals and rare earth ions, whose effect can be a further improvement of the performance of the catalyst in terms of conversion, selectivity and half-life of the catalyst itself. Preferred examples of these optional ingredients are Ba, Ca, Sr, Li, K, Cs and rare earths (La, Ce, Pr), all in ionic form.

The catalyst based on iron and magnesium can be prepared according to any method suitable to facilitate the development of a chemical interaction between the two metals.

It has in fact been found surprisingly that the consequence of this chemical interaction is that the simultaneous presence of the two components leads to a catalyst that is characterized by an unexpectedly better performance than the two individual metals (whatever their physical and chemical form) or in mixtures in which said chemical interaction does not occur.

The expression "chemical interaction" is used to designate the establishment of any synergistic interaction between the two components, magnesium and iron, i.e., such that the catalytic effect due to the simultaneous presence of the two elements cannot be explained with the simple sum of the effects of the two components considered individually.

Preferred examples of chemical interaction according to the present invention are the forming of intermetallic compounds, interoxides with definite or undefined stoichiometry, and the forming of interstitial or substitutional solid solutions.

The preferred methods for preparing said catalyst containing iron and magnesium allow reactions, optionally in the solid state, among the raw materials containing iron and magnesium. These methods include precipitation and mechanical mixing. Preferably, this precipitation is coprecipitation. Equally preferably, this mechanical mixing comprises ball milling and high-energy milling. Preferably, the cited methods are applied to

oxides of iron and magnesium.

In greater detail, the preparation methods comprise techniques for precipitation from aqueous or alcohol solutions containing the cations of the two metals and the corresponding anions depending on the type of salt or compound used as raw material. The precipitation technique is a particularly preferred method, since it allows to obtain samples that are more active and selective than other techniques. One possible explanation, albeit a purely speculative one which as such is not binding, is that this method allows to develop a better chemical interaction between the two elements already at the level of the precursors.

As an alternative, it is possible to use mechanical mixtures of the oxides of the two metals, such as for example Fe_2O_3 and MgO , which when treated appropriately at high temperatures form the catalyst by means of solid state reaction and ion migration effects.

It has been found that catalysts comprising Fe/Mg/O are unexpectedly active and selective in the generic alkylation of 1-naphthol and are particularly advantageous in the methylation of 1-naphthol with methanol to obtain therefore 2-methyl-1-naphthol.

The combination of iron and magnesium plays a fundamental role in optimizing the activity and selectivity characteristics of the catalyst. Moreover, the reactivity of the Mg/Fe/O catalytic system according to the invention is higher than that of conventional basic systems, such as systems using Mg/Al/O , and higher than that of conventional catalysts based on Mg/Fe/O that provide, for example, for the simple mixing of the metals.

Moreover, without intending to be bound to a particular theory, the inventors believe that the surprisingly conspicuous superiority of the present catalyst based on Mg/Fe/O for the reaction of methylation of 1-naphthol to 2-methyl-1-naphthol probably derives from a better selectivity in the product of interest and from a better conversion of the substrate, aspects which may

perhaps be due to the establishment of particular interactions between the aromatic substrate and the surface of the catalyst.

The catalyst can be used as is or, as an alternative, be deposited on an inert medium constituted by silica, alumina, silicoaluminates or any other material suitable to disperse the active phase.

Among the advantages that derive from the use of an inert medium, it is worth mentioning the reduction of the cost of said catalyst (since a lower quantity would be used), the possibility to give the catalyst a larger surface area, and the improvement of the reaction heat dispersion properties.

Finally, the catalyst can be used in the most suitable shapes, such as for example a format constituted by perforated pellets, extruded elements, or a format constituted by spheroidal particles suitable to be used optionally also in a fluid or circulating bed.

Experimental tests to which the catalyst according to the present invention has been subjected have shown that as a consequence of certain optional specific treatments it is possible to vary significantly some functional characteristics of said catalyst.

First of all, advantageously, after its preparation but prior to its use, the catalyst according to the present invention can be subjected to a thermal treatment of the "conventional" type performed in an atmosphere of air, at a temperature not higher than 450 °C. This treatment is within the category of thermal treatments usually performed for all catalysts and corresponds to the one that will be described in examples 7-10 and in comparison example 17.

Secondly, further experimental tests have shown that in some cases the catalyst used here has an unstable initial reactivity, which however stabilizes within at most 20-40 hours.

In such cases, it has been found that a treatment on the catalyst in a nitrogen current, at a temperature between 350 and 450 °C, preferably 450 °C, has unexpectedly led to interesting improvements.

This treatment can be performed (i) on the catalyst samples after a thermal treatment in air of the conventional type (i.e., before the reactivity tests, as will be described in example 14), (ii) on the samples during equilibration (i.e., during the initial period of unstable catalytic behavior, which lasts 20-40 hours), or (iii) after completion of the equilibration step (as in examples 11-12).

The unexpected effect of this treatment seems to be dual: it accelerates the equilibration step and it leads to better performance for the equilibrated catalyst with respect to the sample treated conventionally, i.e., only in air at temperatures below 450 °C. The acceleration of the equilibration step achieved surprisingly with the treatment in nitrogen is difficult to explain and in any case is totally unexpected.

Among the results achieved with the treatment described above, it is worth noting:

- the reduction of the time required to reach the situation of stable catalytic behavior (when this treatment is performed preventively or during the initial period of unstable performance),

- the reduction of the conversion of 1-naphthol, which however is usually compensated by an equivalent or greater increase in selectivity for the intended product (a particularly conspicuous aspect in the case of methylation to 2-methyl-1-naphthol), with consequent increase of the yield in the intended product (regardless of when the treatment is performed). The advantage, however, is not always achieved, since it depends to a certain extent on the conditions in which the reaction is performed.

The experimental results achieved have shown that in a treatment performed on an active catalyst that is characterized by a conversion close to 100% and is very selective, the drop in conversion cited in the second item above is not compensated by an equivalent increase in selectivity (since the selectivity of the untreated catalyst is already very high). In this case there is,

therefore, a slight drop in yield, although said drop can be compensated with an increase in the reaction temperature.

Vice versa, however, when the treatment is performed on an extremely active catalyst (i.e., a catalyst that already converts the reagent completely at the chosen reaction temperature), the conversion drop is small or even negligible, while the increase in selectivity is significant, and therefore there is an increase in yield.

Without binding oneself to particular theories, one may conjecture that this treatment entails a change in the characteristics of a non-equilibrated catalyst and that this change is then maintained during the reaction, so that the performance then remains constant. It is also possible that the treatment with N_2 induces a partial reduction of the iron of the surface of the non-equilibrated catalyst (i.e., with conversion of part of the Fe^{3+} into Fe^{2+}). Currently it is impossible to surmise why an equilibrated catalyst has a better performance if it is treated with this procedure.

To conclude, the treatment can have a different effect depending on the functional state of the treated catalyst, but in any case it leads to an increase in selectivity, which is matched by an increase in yield.

For the specific conversion of 1-naphthol to 2-methyl-1-naphthol, it has been found that the optimum catalytic performance of the catalysts containing iron and magnesium described in the present invention are as follows.

The reaction temperature can be comprised between 300 and 500 °C, preferably comprised between 350 and 450 °C.

The feed ratio between methanol and naphthol is comprised, by way of indication, between 1/1 and 50/1 (expressed as molar ratio between the two reagents), preferably between 3/1 and 20/1.

The total contact time, understood as the ratio between the volume of catalyst and the total volumetric flow-rate of the system comprising vapor,

gas, reagents and carrier gas (for example molecular nitrogen), can be comprised between 0.1 seconds and 100 seconds (measured in normal conditions), preferably between 1 and 10 seconds.

The molar ratio (volumetric) between reagents (methanol and naphthol) in the vapor phase and the total feed to the reactor (reagents and carrier gas) can be comprised between 5 and 80%, preferably between 10 and 40%.

Likewise, total pressure can be comprised between 0.1 absolute atm and 50 absolute atm, preferably comprised between 1 and 10 absolute atm.

Although there is extensive scientific and patent literature on the alkylation of aromatic substrates and in particular on the methylation of phenols, naphthols and derivatives thereof, in all known processes the conversion of the initial product never reaches values that are truly close to 100%. This entails that in order to be able to use alkylated compounds as substrates of additional reactions, it is necessary to purify beforehand the obtained alkylated product. Although this purification can be performed by virtue of methods that are well-known to any person skilled in the art, it nonetheless entails an expenditure in terms of time and cost.

The alkylation process described here instead allows to improve yield and conversion, thus allowing the use of alkylated 1-naphthols as substrates of subsequent chemical processes. The improvement in yield and conversion acquires an entirely particularly value from the standpoint of utilization of said alkylation method within a synthetic strategy for preparing menadione.

From what has been described above, according to a particularly preferred embodiment, the oxidation process of the present invention is applied advantageously to 1-naphthols alkylated as above, i.e., to 1-naphthols alkylated with primary or secondary, linear or side-chain aliphatic alcohols with 1 to 6 atoms of carbon in the hydrocarbon chain.

The process according to this combination of the two steps of alkylation and oxidation comprises the steps of:

a3) placing in contact a mixture that comprises an alcohol and 1-naphthol with a catalyst that contains a mixed oxide of Mg and Fe, said catalyst being prepared from raw materials chosen from salts and oxides of iron containing ferric and ferrous ions and salts and oxides of magnesium,

5 b3) recovering the alkylated product of step a3) without performing methods for separating said product from byproducts and from the initial unreacted aromatic substrate;

where steps a3) and b3) precede steps a1) — d1) of the redox process according to the invention, and

10 where the product recovered from step b3) is said organic compound that can be oxidized in step a1) of the redox process according to the invention.

A preferred embodiment of the combination cited above consists of a process for the synthesis of menadione starting from 1-naphthol. In this case, the alcohol to be used in the alkylation step is methanol, so that the product
15 recovered in step b3) is 2-methyl-1-naphthol.

The characteristics described earlier regarding exemplifying and non-limitative embodiments of the oxidoreduction process and of the alkylation process that can be advantageously concatenated thereto have not been repeated also for the process that comprises the combination of said
20 processes merely to protect the brevity of the application. However, it is evident to the person skilled in the art that these preferred characteristics can be applied easily and advantageously to the two processes of alkylation and oxidoreduction even if they are combined in a single synthetic strategy.

Using as substrates of the oxidoreduction process according to the
25 invention the 1-naphthols alkylated according to the alkylation process cited above means being able to avoid the forming of large quantities of byproducts, together with the depletion of the initial substrate, drastically reducing the potential interference caused by the presence of other molecules. This renders unnecessary all the purification and extraction

passages (for example for the non-alkylated reagent or the byproducts) that up to now prevented direct use of the reaction mix as a new substrate of a second process.

One preferred and advantageous embodiment of this "inline" method is provided if it is applied to the synthesis of menadione, since differently from any hypothetical combination of known alkylation and oxidation processes, it allows to associate a step of highly selective and complete methylation of 1-naphthol with a selective oxidation of the 2-methyl-1-naphthol.

Furthermore, the possibility to easily restore the effectiveness of the oxidizing catalyst (polyoxometalate) of the oxidoreduction step in very bland and fast conditions, together with the possibility to control the rates of all synthetic passages involved, allow to provide a single process for "inline" synthesis of menadione starting from 1-naphthol that is repeated for several production cycles with unchanged yields and selectivities simply by maintaining an adequate and constant feeding of the initial aromatic organic substrate (i.e., 1-naphthol).

Other advantages of the present invention will become better apparent from the following exemplifying but nonlimitative description of particularly preferred examples.

Example 1

(Synthesis of 2-methyl-1,4-naphthoquinone with $H_5PMo_{10}V_2O_{40}$)

Step 1: 1 gram of 2-methyl-1-naphthol is dissolved in 100 ml of n-hexane, through which nitrogen has been bubbled beforehand. 100 g of solution of heteropolycompound 0.4M, (density 1.48 g/ml) having the composition $H_5PMo_{10}V_2O_{40}$ (for the sake of simplicity, the molecules of water of crystallization and hydration are not shown), are placed in a 500-ml reactor and heated to the temperature of 50 °C under vigorous agitation, while nitrogen is bubbled through. The molar ratio between heteropolycompound and substrate is equal to 4.

By means of a suitable funnel, the solution of 2-methyl-1-naphthol is dripped at a constant rate, with the reactor kept at 50 °C and under a nitrogen head, into the solution of heteropolyc compound, under continual agitation. The drip time is equal to approximately 2 hours. At the end, the reaction mixture is kept under agitation for another 10 minutes. The mixture is cooled to 20 °C and the two phases are separated according to the procedure described hereafter.

The light organic phase is washed with water (the wash water is collected in the heavy aqueous phase) in order to remove the traces of heteropolyc compound, while the heavy aqueous phase is washed with n-hexane and then collected in the light phase. The organic phase is anhydriified with Na₂SO₄, filtered and evaporated until a yellow solid product is obtained. The heavy phase is treated further with chloroform and evaporated until a reddish residue is obtained. The two solid residues were dried in a stove at 40 °C for 12 hours and then analyzed to determine the content of menadione by HPLC and GC.

For the sake of completeness of information, the analytical methods are described hereafter:

1. Determination of initial 2-methyl-1-naphthol after the synthesis stage is performed with HPLC: acetonitrile/water as eluent phase, pH 2 from H₃PO₄, flow 1.5 ml; UV/Vis detector at λ 295 nm; Brownlee 5 μ m ODS column; injected volume 20 μ l (from loop); methanol as solvent.
2. Determination of residual 2-methyl-1-naphthol and 2-methyl-1,4-naphthoquinone after synthesis reaction is performed by HPLC, with the same procedure described above, but with UV/Vis detector λ 240 nm.
3. Determination of residual 2-methyl-1-naphthol and 2-methyl-1,4-naphthoquinone after synthesis reaction is performed by GC (internal standard method): PYE Unicam PU 4550, 1.83 m glass column, with 1/4" outside diameter, 2 mm inside diameter, filled with stationary phase

of 5% XE-60 on Chromosorb 100-120 W-AW-DMCS; detector FID, T 180 °C.

The yield in 2-methyl-1,4-naphthoquinone is calculated as the ratio between the molar quantity of recovered product in the two residues and the molar quantity of reagent introduced. The ratio between the weight of recovered 2-methyl-1,4-naphthoquinone and the weight of products other than 2-methyl-1,4-naphthoquinone (present in the two solid residues) is also calculated.

Analyses provide a yield value in 2-methyl-1,4-naphthoquinone equal to 79.9%, for a total conversion of the reagent 2-methyl-1-naphthol. The menadione/resins weight ratio is equal to 6.5%. These values are comparable to those available in the literature.

A fraction of the residual aqueous phase was then used to determine the degree of reduction (α_V) of the vanadium = V^{IV}/V_{tot} (atomic ratio) %. The degree of reduction of the vanadium is determined analytically by potentiometric titration with a platinum electrode. The resulting value for α_V is $47.4 \pm 2.0\%$, in agreement with the value expected from the stoichiometry of the reaction.

The test was repeated in order to determine the degree of reproducibility of the reaction and the degree of reliability of the analytical method, and provided the following results: yield in 2-methyl-1,4-naphthoquinone equal to 81.9%, for a total conversion of the reagent 2-methyl-1-naphthol. The menadione/resins weight ratio is $6.3 \alpha_V$, equal to $50.0 \pm 2.0\%$.

The concentration of the heteropolycompound in the aqueous solution is equal to 1.09% vanadium by weight; the solution is then treated with pure O_2 at atmospheric pressure and at the temperature of 100 °C (step 2). After 13 hours of treatment, the value of α_V is determined again and is found to be equal to $25.5 \pm 2.0\%$. At this point the solution is concentrated by removing the solvent at the temperature of 100 °C, until a concentration of

heteropolycompound equal to approximately 2.5% by weight of vanadium is obtained.

The aqueous solution is replenished with fresh heteropolycompound in an amount that corresponds to the amount used to determine the value of α_v .

5 Clearly, if this operation is not necessary this determination is not performed.

The synthesis stage is then repeated, using the same aqueous solution containing the regenerated heteropolycompound, which has an α_v equal to $25 \pm 2.0\%$, and repeating the procedure as in step 1 (step 3). The result is a
10 yield value in 2-methyl-1,4-naphthoquinone equal to 79.2%, for a total conversion of the reagent 2-methyl-1-naphthol.

The value α_v is then determined again and is found to be equal to $67.2 \pm 2.0\%$.

The aqueous solution is then subjected to a reoxidation treatment again,
15 as in step 2 (step 4). The aqueous solution containing the partially regenerated heteropolycompound (initial α_v equal to $25 \pm 2.0\%$) is reused again (steps 5 onward).

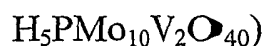
The result is a yield in menadione equal to 78.0%, with a ratio between weight of menadione and weight of resins equal to 4.3 and a degree of
20 reduction α_v at the end of the reaction equal to $66.7 \pm 2.0\%$.

These tests therefore demonstrate that it is possible to use several times the heteropolycompound between α_v equal to 20-30% and α_v equal to 60-75%, achieving each time a menadione yield comprised between 78% and 80%.

25

Example 2 (comparative)

(Synthesis of 2-methyl-1,4-naphthoquinone with concentrated



The procedure described in Example 1 is repeated, except that after step 1 and prior to step 2, the solvent is evaporated at 100 °C in order to obtain a

concentration of heteropolycompound in aqueous solution similar to the one used for the first reduction, equal to approximately 2.5% by weight of vanadium on 100 g of solution. In this specific example, a concentration of V equal to 2.46% by weight is reached. The treatment of this solution to reoxidize the vanadium to a value of α_V equal to approximately 25-30% is extended for 52 hours in this case. The advantage that can be achieved by performing the reoxidation treatment on the diluted solution is therefore evident.

Example 3

10 (Synthesis of 2-methyl-1,4-naphthoquinone with $H_4PMo_{10}V_1O_{40}$)

The reduction procedure described in Example 1 is repeated, except that a heteropolycompound having the composition $H_4PMo_{10}V_1O_{40}$, with a molar ratio of 4 between the heteropolycompound and the substrate, is used. The resulting menadione yield is equal to 67.3%, with a ratio between weight of menadione and weight of resins equal to 3.2 and with total conversion of the substrate. The value of α_V is equal to $81.8 \pm 2.0\%$.

This test demonstrates that it is possible to use a heteropolycompound containing a single atom of V by formula, and that it can be reduced almost completely. In these conditions, however, the resulting yield is considerably lower than the yield obtained in Example 1.

The treatment of concentration of the aqueous solution containing the reduced heteropolycompound was then performed until a solution containing 1.19% V was obtained. This was then subjected to the treatment of reoxidation with oxygen, and after 29 hours of treatment a degree of reduction α_V equal to $77.0 \pm 2.0\%$ was reached; extension of the treatment in the same conditions did not provide further variations of the degree of reduction.

This test demonstrates that the catalyst containing a single atom of V by molecular formula can be used as oxidizer, but is then found to be an

ineffective reducing agent for molecular oxygen, and therefore is less effective than the compound containing 2 atoms of V by molar formula.

Example 4

(Synthesis of 2-methyl-1,4-naphthoquinone with $H_5PMo_{10}V_2O_{40}$ under pressure at high temperature)

The reduction procedure (step 1) described in Example 1 is repeated, but step 2 is performed at high pressure (10 atmospheres of pure O_2) in an autoclave at 120 °C. After 12 hours of treatment, the value α_V is equal to 12%. The value of the yield in 2-methyl-1,4-naphthoquinone is equal to 75.9%, with a menadione/resins ratio equal to 5.63 at the 3rd cycle. If step 2 is instead performed in the same conditions used in Example 1, at least 150 hours of treatment are needed in order to reach a value of α_V lower than 5%.

It is therefore evident that the use of a fully reoxidized catalyst would lead to times (or reaction conditions) for the redox process that are inapplicable from the industrial standpoint.

Example 5

(Synthesis of 2-methyl-1,4-naphthoquinone with $H_5PMo_{10}V_2O_{40}$ with extended dripping)

The procedure described in Example 1 is repeated, except that the dripping time of the solution containing the reagent in the aqueous solution is equal to 210 minutes. The result is a significant increase in the yield in 2-methyl-1,4-naphthoquinone, which is equal to 88%.

Example 6

(Synthesis of 2-methyl-1,4-naphthoquinone with $H_5PMo_{10}V_2O_{40}$ and heteropolycompound/substrate ratio equal to 2)

The procedure described in Example 1 is repeated, except that a ratio between heteropolycompound and substrate equal to 2 instead of 4 is used. The result is a menadione yield equal to 74.1%, with a ratio between weight of menadione and weight of resins equal to 5.7 and with total conversion of

the substrate. The value of α_V is equal to $88.9 \pm 2.0\%$.

This test demonstrates that it is possible to reduce both atoms of vanadium present in the heteropolycompound, but the yield in menadione is lower than in Example 1, with a higher ratio between heteropolycompound and substrate and with a final degree α_V equal to approximately 40-50%.

A reoxidation procedure similar to the one described in comparison in Example 1 is then applied, providing first an evaporation of the solvent in order to increase the concentration of the heteropolycompound until a concentration of 2.39% of V is reached, and then a treatment with oxygen at atmospheric pressure and at 100 °C, which over 44 hours leads to a partial reoxidation of the vanadium, achieving a value of α_V equal to $27.9 \pm 2.0\%$.

This example points out that the optimum molar ratio between heteropolycompound and substrate, when the heteropolycompound is constituted by $H_5PMo_{10}V_2O_{40}$, is equal to approximately 4, since it is possible to achieve time optimization by varying the value of α_V between a minimum equal to 70-80% and an initial maximum equal to 20-30%.

The preparation of the catalysts containing iron and magnesium described in the examples that follow was performed according to the following method: a weighed amount of $Mg(NO_3)_2 \cdot 6H_2O$ and of $Fe(NO_3)_3 \cdot 9H_2O$ is dissolved in demineralized water so as to provide a homogeneous solution of the cations Mg^{2+} and Fe^{3+} in a chosen atomic ratio. The dissolved quantity might correspond, for example, to the provision of a 1 M concentration of the cations. For example, in a volume of 167 ml of H_2O , 21.39 g of magnesium salt and 33.71 g of iron salt are dissolved so as to provide a final atomic ratio of $Mg/Fe = 1/1$. 22.33 g of Na_2CO_3 are dissolved separately in 209 ml of demineralized water. The first solution is dripped into the second one, keeping the temperature at 50 °C and under agitation and the pH of the solution equal to approximately 10 (the pH is kept constant by adding NaOH

3M). The result is a precipitate, and slurry digestion is allowed for approximately 40 minutes. The precipitate is then filtered and washed with abundant demineralized H₂O (for example 3-7 liters) kept at 40 °C. The precipitate is first dried at 90 °C for one night and then subjected to heat treatment by gradual heating, raising it from ambient temperature to a final temperature that can be comprised between 450 °C and 800 °C, preferably between 450 °C and 650 °C, even more preferably 600 °C. The thermal gradient can be the one used typically in industrial practice, and the heat treatment atmosphere can be constituted by a gas such as air, nitrogen, oxygen or other inert gas used in industrial practice, in a flow of said gas or in static conditions.

This heat treatment has the prerogative of being performed at high temperatures and has unexpectedly allows to obtain a catalyst with higher performance (as shown more clearly in Example 11), even higher than the performance achievable with a treatment in nitrogen at temperatures lower than 450 °C, such as the one described earlier in the present application.

The reason for this superiority is currently not absolutely clear. A mere hypothesis may be that a better defined crystalline structure containing the ferrous ion forms at high temperatures.

The different effects of these two last treatments are compared better in examples 11 and 13.

The final temperature is maintained for 8 hours. The procedure described above leads to the obtainment of 10 g of catalyst. Quantities proportional to the cited values are used in order to obtain different quantities or different Mg/Fe ratios.

This procedure is an example of preparation, but any method that leads to a system in which there is a chemical interaction between Mg and Fe is suitable.

Catalytic reactivity tests were performed in a laboratory reactor with flow

operating at atmospheric pressure, by loading 1 ml of catalyst (loose packing measurement) and feeding a liquid mix of methanol and 1-naphthol prepared so as to have a methanol/naphthol molar ratio equal to 10:1. These tests were performed at 390 °C, although lower temperatures were used in some cases.

5 The liquid mix was injected by means of a pump at a rate equal to 0.36 ml per hour and then vaporized in a hot line, where it was collected by a carrier gas constituted by nitrogen and carried to the flow reactor. The flow rate of the carrier gas is equal to 20 ml/min. The overall current in vapor/gas phase has a flow rate equal to 24 ml/min, when measured at 20 °C and at
10 atmospheric pressure; a contact time equal to 2.5 seconds is therefore provided.

The current in output from the reactor is first cooled and then bubbled through two scrubbers containing acetone. The collection of the reaction products is extended for a definite time (typically 1 hour). The mixture of the
15 reaction products, dissolved in acetone, is then analyzed by gas chromatography by using an HP-5 column, in which the temperature was set from 100 °C (5 min) to 250 °C with a heating gradient of 5 °/min. The final temperature was maintained for 30 minutes. The reported data (yields, conversion, selectivity) are to be understood as calculated on a molar basis.

20

Example 7

(Catalyst containing iron and magnesium with Mg/Fe ratio equal to 0.05)

A catalyst is prepared according to the method described above and is finally subjected to thermal treatment in air at 450 °C. The sample is characterized by a Mg/Fe ratio, expressed as atomic ratio between the two
25 elements, equal to 0.05. Conversion of the 1-naphthol is equal to 74%, while selectivity to 2-methyl-1-naphthol is equal to 85%.

Example 8

(Catalyst containing iron and magnesium with Mg/Fe ratio equal to 0.25)

A catalyst is prepared according to the method described above, and is

finally subjected to heat treatment in air at 450 °C. The sample is characterized by a Mg/Fe ratio, expressed as atomic ratio between the two elements, equal to 0.25. The conversion of 1-naphthol is found to increase and is now equal to 98%. Despite the high conversion, there is also high selectivity to 2-methyl-1-naphthol, which is equal to 92%.

Example 9

(Catalyst containing iron and magnesium with Mg/Fe ratio equal to 0.75)

A catalyst is prepared according to the method described above, and is finally subjected to heat treatment in air at 450 °C. The sample is characterized by a Mg/Fe ratio, expressed as atomic ratio between the two elements, equal to 0.75. A further increase of 1-naphthol conversion is observed; conversion is now equal to 100%. However, there is a slight decrease in selectivity to 2-methyl-1-naphthol, which is now equal to 81%.

Example 10

(Catalyst containing iron and magnesium with Mg/Fe ratio equal to 1.50)

A catalyst is prepared according to the method described above, and is finally subjected to heat treatment in air at 450 °C. The sample is characterized by a Mg/Fe ratio, expressed as atomic ratio between the two elements, equal to 1.5. Conversion of 1-naphthol equal to 99% is observed. Selectivity to 2-methyl-1-naphthol is equal to 78%.

Example 11

(Catalyst with Mg/Fe ratio equal to 0.05 subjected to treatment in nitrogen at 450 °C)

The catalyst described in Example 9, once the stable catalytic performance cited in the example has been reached, is subjected to treatment in a current of N₂ at 450 °C for 3 hours. After this treatment, the performance is as follows: 1-naphthol conversion 98%, selectivity to 2-methyl-1-naphthol 96%. The treatment therefore produces, with respect to the stationary situation described in Example 9, a slight decrease of

conversion but a considerable increase in selectivity. The yield of the chosen product (given by the product of conversion and selectivity) is therefore distinctly higher than the yield obtained before said treatment. The same result is achieved if the pretreatment is performed on the fresh catalyst, i.e.,
5 after calcinations in air.

Example 12

(Catalyst with Mg/Fe ratio equal to 1.50 subjected to treatment in nitrogen at 450 °C)

The catalyst described in Example 10, after reaching the stable catalytic
10 performance cited in the example, is subjected to a treatment in N₂ current at 450 °C for 3 hours. After this treatment, the performance is as follows: 1-naphthol conversion 98%, selectivity to 2-methyl-1-naphthol 95%. The treatment therefore leads, with respect to the stationary situation described in Example 10, to a negligible decrease in conversion but to a substantial
15 increase in selectivity. The yield in the chosen product (determined by the product of conversion and selectivity) is therefore distinctly higher, in this case also, than before this treatment.

Example 13

(Catalyst with Mg/Fe ratio equal to 0.05 subjected to treatment in air at 600 °C)

20 The catalyst is prepared as described in Example 9, but instead of being subjected to a heat treatment at 450 °C in air, it undergoes a treatment at 600 °C in air for 3 hours. After this treatment, the catalyst shows the following improvements with respect to the sample described in Example 9: shorter time required to reach stable performance and distinctly higher catalytic
25 performance than the catalyst described in Example 9, especially in terms of selectivity: 1-naphthol conversion 100%, selectivity to 2-methyl-1-naphthol equal to 96%.

Example 14

(Catalyst with Mg/Fe ratio equal to 2.00 subjected to preventive treatment in

nitrogen at 450 °C)

A catalyst is prepared according to the method described above, and is finally subjected to heat treatment in air at 450 °C. However, differently from the catalysts described in Examples 7-13, the catalyst is also subjected to a preliminary treatment at the same temperature in a nitrogen current before starting the reactivity tests. The sample is characterized by a Mg/Fe ratio, expressed as atomic ratio between the two elements, equal to 2.0. Conversion of 1-naphthol equal to 92% is observed. Selectivity to 2-methyl-1-naphthol is equal to 90%.

This example shows how much treatment with nitrogen can have a positive effect on the performance of the catalyst. Although the trend of the results mentioned so far could lead one to expect that an atomic ratio of 2 between the two metals would produce a modest result, a total yield equal to 82.8% (with 90% selectivity) exceeds considerably the values related to the situation described in Example 10 (in which the calculated yield is 77.2%), in which the lower atomic ratio (equal to 1.5) should have instead led to better results.

Example 15 (comparative)

(Catalyst containing only Fe₂O₃)

A catalyst is prepared according to the method described above, and is finally subjected to heat treatment in air at 450 °C. The sample does not contain magnesium and is therefore constituted solely by Fe₂O₃. One obtains a conversion of 48%, with selectivity to 2-methyl-1-naphthol equal to 84%. The byproducts are essentially constituted by 4-methyl-1-naphthol and by products of methylation of the aromatic ring.

Example 16 (comparative)

(Catalyst containing only MgO)

A catalyst is prepared according to the method described above, and is finally subjected to heat treatment in air at 450 °C. The sample does not

contain iron, and therefore is constituted only by MgO. One obtains 42% conversion, with selectivity to 2-methyl-1-naphthol equal to 74%. The byproducts are essentially constituted by 4-methyl-1-naphthol and by products of methylation of the aromatic ring.

Example 17 (comparative)

(Catalyst with Mg/Fe ratio equal to 0.25 from simply mixed Fe_2O_3 and MgO)

A catalyst is prepared by using the following method: first Mg and Fe hydroxates are precipitated separately; then, they are filtered separately and dried at 90 °C. The two precipitates are then simply mixed so as to have a Mg/Fe atomic ratio equal to 0.25, and the mixture is treated as usual at 450 °C for 8 hours in air. The catalyst yields the following performance: conversion 36%, selectivity 84%. Accordingly, the catalyst is less active than the corresponding sample prepared with the coprecipitation method.

Comparison example 15 and comparison example 16 show that the two oxides (Fe_2O_3 and MgO) considered individually offer a markedly worse catalytic performance than catalysts containing both components (Mg/Fe/O). It is therefore evident that there is a synergistic effect that derives from a chemical interaction between the two ions in the mixed oxide.

Furthermore, the values of conversion and selectivity of comparison example 17 (which describes a conventional catalyst based on Fe and Mg) show that the co-presence of the two metals is not sufficient to provide what has been defined as a "chemical interaction" between the two elements. The simple mixing of the oxides is in fact not sufficient to provide the performance that can be obtained with a catalyst that is instead prepared according to the method of the present invention.

The synergy cited above is even more evident from analysis of the following table, which compares the data of the described examples.

The comparison is particularly important if it relates to the data of

Example 15, in which the catalyst was constituted by ferric oxide alone, to Example 16, in which only magnesium was used, to Example 17, in which the two oxides were used together in such quantities that the atomic ratio between magnesium and iron was equal to 0.25 but were mixed
 5 ineffectively, and to Examples 7 and 8. The first of these two last examples is the worst experimental result achieved, but was obtained by using a catalyst prepared according to the present invention. However, even in this case the final yield values are significantly better than the ones related to the three cases of Examples 15, 16 and 17.

10 Example 8 is instead particularly significant, since despite having a ratio between the quantities of the two metals equal to comparison example 17 (i.e., equal to 0.25), it allows to achieve unexpected excellent results by virtue of the fact that the two elements have not been simply mixed physically but have been used as taught by the present invention.

CATALYST	CONVERSION	SELECTIVITY	YIELD
(example 7) Mg/Fe = 0.05	74%	85%	63%
(example 8) Mg/Fe = 0.25	98%	92%	90%
(example 9) Mg/Fe = 0.75	100%	81%	81%
(example 10) Mg/Fe = 1.50	99%	78%	77%
(example 11) Mg/Fe = 0.75 + N ₂ 450 °C	98%	96%	94%
(example 12) Mg/Fe = 1.50 + N ₂ 450 °C	98%	95%	93%
(example 13) Mg/Fe = 0.75 + air 600 °C	100%	96%	96%
(example 14) Mg/Fe = 2.00 + N ₂ 450 °C	92%	90%	83%
(example 15) Fe ₂ O ₃	48%	84%	40%
(example 16) MgO	42%	74%	31%
(example 17) MgO + Fe ₂ O ₃	36%	84%	30%

15 It has also been noted subsequently that the performance achieved in Example 14 was in any case lower than in Example 12. This result is very

significant, since both examples provided for treatment in nitrogen at 450 °C. Therefore, the comparison points out that the preferred Mg/Fe ratio is between 0.05 and 1.5.

5 The difference in performance becomes even more significant by comparing the data related to Example 14 with the data, for example, of Examples 11 and 13, in which the Mg/Fe ratio is markedly lower than 1.

10 The identification of a preferred range of magnesium and iron ratios is also supported by the fact that with reference to the comparison cited above between Example 14 and Examples 11 and 13, the first example (14) has also been subjected to a treatment in nitrogen which inherently entails an improvement of the result that would be achieved otherwise.

The disclosures in Italian Patent Applications No. MI2002A001762 and MI2003A000809 from which this application claims priority are incorporated herein by reference.

CLAIMS

1. A redox process for preparing an oxidized organic compound, comprising the steps of:

a1) reacting an oxidizable organic compound chosen among phenols, naphthols and optionally substituted derivatives thereof, with one or more polyoxometalate compounds having the general formula



where

Me is a metal ion chosen from the group that comprises Na^+ , K^+ , Li^+ , Cs^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Al^{3+} , Fe^{3+} , La^{3+} , Ce^{3+} , Cr^{3+} , or a combination thereof;

a is the valence of Me,

m is comprised between 0 and 7 depending on a and n;

n is comprised between 1 and 4,

p is comprised between 0 and 6,

said polyoxometalate compounds being characterized in that the average oxidation number calculated on the total atoms of vanadium is greater than 4,

b1) recovering the organic product of the reaction of a1),

c1) restoring the average oxidation state of the vanadium in said polyoxometalate compounds, so that it is comprised between 4 and 4.95, reacting said polyoxometalate compounds with a compound that has a lower oxidation potential than said polyoxometalate compounds,

d1) repeating one or more times the three preceding steps, using the product of c1) as polyoxometalate compound in the subsequent steps a1).

2. The process according to claim 1, wherein said oxidizable organic compound is 2-methyl-1-naphthol.

3. The process according to claim 1, wherein said organic compound is present in concentrations equal to at most 0.1M.

4. The process according to claim 1, wherein at least one of said

polyoxometalate compounds is $H_5PMo_{10}V_2O_{40}$, alone or mixed with others.

5. The process according to claim 1, wherein said polyoxometalate compounds are present in concentrations that vary between 0.02M and 0.5M.

6. The process according to claim 2, wherein the molar ratio between the
5 moles of polyoxometalate and of 2-methyl-1-naphthol is equal to 4:1.

7. The process according to claim 1, wherein said step a1) occurs at a temperature between 25 °C and 100 °C.

8. The process according to claim 1, wherein said polyoxometalate compounds are added to said organic compound in a time interval that varies
10 between 0.5 and 8 hours.

9. The process according to claim 1, wherein in step c1) said average oxidation state of the vanadium is restored to a value comprised between 4.60 and 4.90.

10. The process according to claim 1, wherein step c1) occurs at a
15 temperature comprised between 80 °C and 110 °C.

11. The process according to claim 1, wherein in step c1) the concentration of said polyoxometalate compounds is lower than 2% by weight with respect to the total weight of the solution that contains them.

12. The process according to claim 1, wherein step c1) has a duration
20 comprised between 0.5 hours and 15 hours.

13. The process according to claim 1, wherein in step c1) said compound having a lower oxidation potential than said polyoxometalate compounds is selected from the group that comprises air, oxygen or mixtures thereof.

14. The process according to one or more of the preceding claims,
25 wherein said step a1) and said step c1) have comparable rates and, together with step b1), constitute a continuous process.

15. The process according to any one of the preceding claims for the oxidation of naphthols and optionally substituted derivatives thereof.

16. The process according to claim 15, characterized in that before steps

a1)-d1) it comprises the steps of:

a3) placing in contact a mixture that comprises an alcohol and 1-naphthol with a catalyst that contains a mixed oxide of Mg and Fe, said catalyst being prepared from raw materials chosen from salts and oxides of iron containing
5 ferric and ferrous ions and salts and oxides of magnesium,

b3) recovering the alkylated product of step a3) without performing methods for separating said product from byproducts and from the initial unreacted aromatic substrate;

wherein the product recovered from step b3) is said oxidizable organic
10 compound in step a1) of claim 1.

17. The process according to claim 16, wherein said alcohol is an aliphatic, linear or branched-chain, primary or secondary alcohol, with 1 to 6 atoms of carbon in the hydrocarbon chain.

18. The process according to claim 17, wherein said alcohol is methanol.

15 19. The process according to claim 18, wherein the feeding of 1-naphthol is constant and steps a3) to d1) constitute an "inline" process for synthesis of menadione that is repeated for several production cycles.

20. The process for preparing of 1-naphthol alkylate, comprising the steps of:

20 a2) placing in contact a mixture that comprises an alcohol and 1-naphthol with a catalyst that contains a mixed oxide of Mg and Fe, said catalyst being prepared from raw materials chosen from salts and oxides of iron containing ferric and ferrous ions and salts and oxides of magnesium,

25 b2) recovering the alkylated product of step a2) without performing methods for separating said product from byproducts and from the initial unreacted aromatic substrate.

21. The process according to claim 20, wherein said alcohol is an aliphatic, linear or branched-chain, primary or secondary alcohol, with 1 to 6 atoms of carbon in the hydrocarbon chain.

22. The process according to claim 21, wherein said alcohol is methanol.

23. The process according to claims 16 and 20, wherein said raw materials are selected from the group that consists of oxides of iron (ferric and ferrous), maghemite, magnetite, hematite, inorganic iron salts, magnesium oxides, inorganic magnesium salts and mixtures thereof.

24. The process according to claims 16 and 20, wherein said catalyst is produced by subjecting said raw materials to precipitation or mechanical mixing.

25. The process according to claim 24, wherein said mechanical mixing comprises ball milling and high-energy milling.

26. The process according to claim 24, wherein said precipitation is coprecipitation.

27. The process according to claims 16 and 20, wherein said catalyst has an atomic ratio between magnesium and iron (Mg/Fe) comprised in a range between 0.01 and 10.

28. The process according to claim 27, wherein said range is comprised between 0.01 and 5.

29. The process according to claims 16 and 20, wherein said catalyst also comprises at least one other element selected from the group that comprises alkaline metal ions, alkaline earth metal ions, transition or post-transition metal ions, rare earth ions, and mixtures thereof.

30. The process according to claims 16 and 20, wherein said catalyst, before being used, is calcinated in an air current at a temperature comprised between 450° and 650° C.

31. The process according to claims 18 to 22, wherein the reaction temperature is comprised between 300 and 500° C.

32. The process according to claims 18 and 22, wherein the feed ratio between methanol and naphthol expressed as molar ratio between the two reagents is comprised between 1/1 and 50/1.

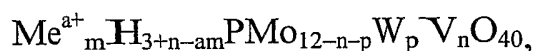
33. The process according to claims 18 and 22, wherein the global contact time is comprised between 0.1 seconds and 100 seconds.

34. The process according to claims 18 and 22, wherein the (volumetric) molar ratio between reagents in the vapor phase and the total feed to the reactor is comprised between 5% and 80%.

35. The process according to claims 18 and 22, wherein the total pressure is comprised between 0.1 absolute atm and 50 absolute atm.

36. The process according to claims 16 and 20, wherein said catalyst is used as is, in suitable shapes, or is deposited on an inert medium suitable to disperse said catalyst.

37. A use of one or more polyoxometalate compounds having the general formula



where

Me is a metal ion selected from the group that comprises Na^+ , K^+ , Li^+ , Cs^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Al^{3+} , Fe^{3+} , La^{3+} , Ce^{3+} , Cr^{3+} , or a combination thereof;

a is the valence of Me,

m is comprised between 0 and 7 depending on a and n;

n is comprised between 1 and 4,

p is comprised between 0 and 6,

as oxidizing agents in reactions for oxidation of organic compounds chosen among phenols, naphthols and optionally substituted derivatives thereof, characterized in that the average oxidation number of the vanadium is comprised between 4 and 4.95.