One-step vapour-phase synthesis of 2-methyl-1-naphthol from 1-tetralone

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Abstract

Two synthetic routes, via 2-methyl-1-tetralone and 1-naphthol were tested to produce 2-methyl-1-naphthol from 1-tetralone. The vapour-phase catalytic reactions of methylation and dehydrogenation proceed with high conversion and selectivity (90–97%) over modified iron oxide and palladium supported on activated carbon, respectively. The reactions were carried out under the similar conditions (T, P, etc.). Methanol was used as a diluent and methylating agent as well. The obtained results allowed to propose a reaction scheme for one-step synthesis of 2-methyl-1-naphthol. The scheme includes two fixed-bed reactors in line or a single reactor with a double-layered or mixed catalytic bed. The main advantage of the proposed scheme is avoiding the intermediate separation and purification steps. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 1-Tetralone; Methylation; Dehydrogenation; 2-Methyl-1-naphthol; Vapour-phase synthesis

1. Introduction

2-Methyl-1-naphthol has considerable promise as an intermediate in the preparation of pharmaceuticals. It can be selectively oxidised to 2-methyl-1,4-naphthoquinone (Menadione, Vitamin K3) by peroxides [1,2]. Menadione is in turn an intermediate in the production of Vitamins K1, K2 and K4. Up to now, a typical process of producing Menadione comprises 2-methylnaphthalene oxidation with chromic acid in liquid phase [3]. The yield of the final product is about 70%. However, it is well known that the use of a large amount of chromium compounds constitutes a serious ecological hazard and gives rise to problems in the treatment of wastewater. Vapour-phase synthesis of 2-methyl-1-naphthol

is free of these disadvantages. The known processes for vapour-phase 2-methyl-1-naphthol production are those utilising as starting materials, 1-naphthol or 1-tetralone. The processes with 1-naphthol comprise gas-phase methylation of 1-naphthol in the presence of the catalysts, such as Al_2O_3 [4,5] and Fe_3O_4 modified by chromium, silicon and potassium [6]. The best result obtained over alumina catalysts was ~40% yield (350 °C) of 2-methyl-1-naphthol. Besides numerous ring alkylated products, the final mixture also contained the products of O-alkylation and dehydroxylation reactions. The reaction of 1-naphthol methylation over modified iron oxide catalyst was characterised by high conversion and selectivity (90% yield of 2-methyl-1-naphthol at 300 °C). No catalyst deactivation was observed during the experiment.

The use of 1-tetralone as a starting material for 2-methyl-1-naphthol production seems to be more attractive due to comparatively low cost of this

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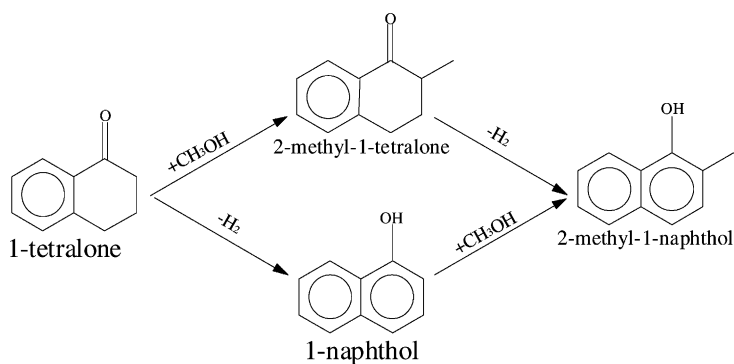
Scheme 1.

substance. The reaction scheme can be presented as shown in Scheme 1.

The scheme consists of two different synthetic routes. The known example of the first process comprises methylation of 1-tetralone over Al$_2$O$_3$ and subsequent dehydrogenation of 2-methyl-1-tetralone in the presence of Pd/C catalyst [7]. However, 1-tetralone can be also converted to 1-naphthol by dehydrogenation over Pd or Ni supported on Al$_2$O$_3$ [8,9] and then, as already described above, 1-naphthol can be methylated giving 2-methyl-1-naphthol [6].

In order to simplify the two-stage vapour-phase synthesis and to avoid intervening product separation we have proposed to connect in line the catalytic reactors used for the different stages. It is also possible to use a single reactor with a two-layered or mixed catalytic bed. Such approach is feasible if the reaction conditions of the methylation and dehydrogenation reactions are the same and the product yields are sufficiently high. The reaction of 1-naphthol methylation over Fe$_3$O$_4$ modified by different ions fulfils this requirement. However, the reactions of methylation and dehydrogenation over the alumina based catalysts described in open literature are characterised by rather low selectivity (50–75%) [4,5,8,9]. Moreover, 2-methyl-3,4-dihydronaphthalene and 1,2-dihydronaphthalene were found to be the main products of 1-tetralone methylation over Al$_2$O$_3$ at 220–350 °C [10]. No traces of 2-methyl-1-tetralone were detected.

The present study is devoted to the investigation of the reactions composing multi-step synthesis of

2-methyl-1-naphthol from 1-tetralone in order to develop one-step vapour-phase process.

2. Experimental

2.1. Reagents and catalysts

Granulated γ-alumina from Engelhard (Al-3982. T1/8, lot no. H-08) was used as a starting material for the Al$_2$O$_3$-based catalysts preparation. All other chemicals (purum quality) were purchased from Fluka (Buch, Switzerland).

Taking into account that the alkylation of 1-naphthol proceeds with high yield and selectivity over modified Fe$_3$O$_4$ [6], this catalyst was also explored for methylation. Iron oxide catalyst containing additives, namely, chromium, silicon and potassium oxides was synthesised by co-precipitation from aqueous solutions of nitrates [6]. The precipitate was separated, washed with water, dried at room temperature and calcined at 470 °C during 5 h. The resulting material was composed of Fe$_2$O$_3$, Cr$_2$O$_3$, SiO$_2$ and K$_2$O in a molar ration of 100:2:1:0.1. The catalyst was crushed and sieved. The fraction with diameter of 0.3–0.5 mm was used for catalytic tests.

γ-Alumina modified by MgO, Li$_2$O and Fe$_3$O$_4$ was investigated in alkylation of 1-tetralone. The catalysts were prepared by wet impregnation of γ-Al$_2$O$_3$ with appropriate aqueous solutions of Mg(NO$_3$)$_2$, LiNO$_3$, Fe(NO$_3$)$_3$. Before impregnation alumina was dried at 200 °C for 2 h. After impregnation and drying at room temperature over night the samples were calcined in air at 650 °C for 8 h.

Table 1
Vapour-phase methylation of 1-tetralone ($m_{cat} = 10$ g; $F_0 = 1.4 \times 10^{-2}$ mol h^{-1}; diluent—MeOH)

Catalyst	T (°C)	Conversion of 1-tetralone (%)	Selectivity to 2-methyl-1-tetralone (%)	Selectivity to 2-methyl-3,4-dihydronaphthalene (%)
Al$_2$O$_3$	270	60	10	31
15 at.%MgO/Al$_2$O$_3$	250	83	62	17
	270	99	27	57
(5 at.%MgO + 5 at.%Li$_2$O)/Al$_2$O$_3$	270	89	74	17
	290	99	35	58
Fe$_3$O$_4$(SiCrK)	270	88	90	–
3.6 at.%Fe$_3$O$_4$/Al$_2$O$_3$	270	97	33	45

Pd supported on activated carbon (0.3–0.5 mm) and on γ-Al$_2$O$_3$ were used as catalysts for dehydrogenation. The catalysts were prepared by wet impregnation of the supports with aqueous ammonia solutions of Pd acetate of appropriate concentration. After drying at room temperature, the samples were calcined in air at 350 °C for 2 h.

All catalysts used in this work are presented in Tables 1 and 2.

2.2. Reaction procedure

The vapour-phase catalytic reactions were carried out in an electrically heated stainless-steel tubular fixed-bed reactor (Fig. 1) under normal pressure. The substrate solution in methanol (methylating agent) or in an appropriate inert solvent (benzene, heptane, etc.) was fed into the reactor using a micro-feed syringe pump. All lines before the reactor were heated up to 150 °C. Reaction temperature was varied in the range of 260–500 °C. To change residence time in the reactor, molar inlet flow rate (F_0) and catalyst mass (m_{cat}) were varied in the range of $1 \times 10^{-2} < F_0 < 1 \times 10^{-1}$ mol h^{-1} and $5 \times 10^{-3} < m_{cat} < 2 \times 10^{-2}$ kg. The reaction products were condensed at the reactor
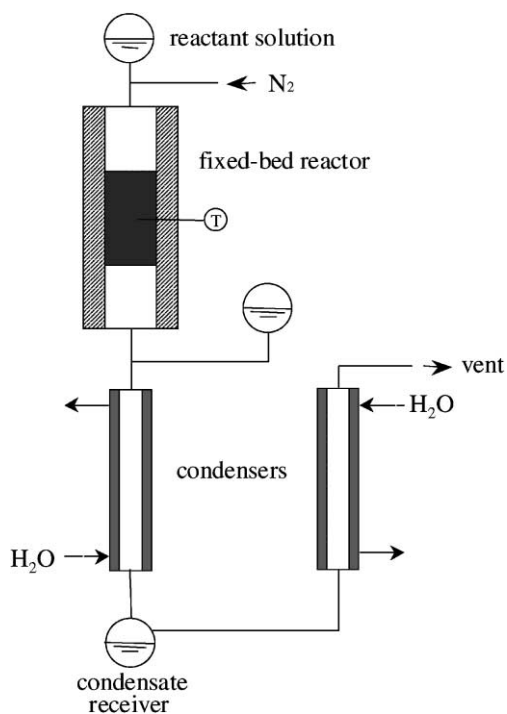

Fig. 1. Scheme of the experimental reactor.

Table 2
Dehydrogenation of 1-tetralone ($m_{cat} = 10$ g; $F_0 = 1.4 \times 10^{-2}$ mol h^{-1})

Catalyst	T (°C)	Diluent	Conversion of 1-tetralone (%)	Yield of 1-naphthol (%)	Selectivity to 1-naphthol (%)
5%Pd/C	290	heptane	64	62	98
5%Pd/C	290	benzene	73	72	99
5%Pd/C	290	methanol	67	65	97
	350	methanol	95	71	75
5%Pd/Al$_2$O$_3$	290	heptane	98	<1	–

outlet and collected for analysis. The product distribution was determined quantitatively by GC analysis (Capillary GC, Perkin-Elmer Autosystem XL, column PE-35).

3. Results and discussion

### 3.1. Vapour-phase methylation of 1-tetralone

The reaction was investigated in the range of temperature from 250 to 350 °C. The mixture of 1-tetralone and methanol (1:20) was fed into the reactor. Based on obtained experimental results, the products of 1-tetralone vapour-phase methylation over used catalysts can be presented as shown in Scheme 2.

The reaction conditions and the results obtained over the different catalysts are summarised in Table 1.

Distribution of the reaction products strongly depends on the catalyst used. In all cases, the main products of 1-tetralone methylation over Al_2O_3 based catalysts were found to be 2-methyl-1-tetralone and 2-methyl-3,4-dihydronaphthalene. While the former is a simple methylation product, formation of the latter involves methylation of 1-tetralone as well as reduction of carbonyl group. These results do not coincide with the reported results of 1-tetralone methylation over Al_2O_3 [10]. The authors observed the formation of 1,2-dihydronaphthalene and 2-methyl-3,4-dihydronaphthalene as main prod-

ucts over sodium-free γ-Al_2O_3. No traces of 2-methyl-1-tetralone were detected under the same reaction conditions. This discrepancy can be explained by different acid-base properties of used alumina catalysts. In order to investigate influence of alumina catalyst acidity on distribution of the final products, the catalysts modified by the basic oxides, i.e. MgO, Li_2O were tested in 1-tetralone methylation. As seen from Table 1, modification of alumina by the basic oxides leads to significant increase of catalytic activity. At the same time, reaction selectivity towards 2-methyl-1-tetralone increases with basicity and decreases with reaction temperature. A certain basicity on the catalyst surface seems to be necessary for the formation of C-alkylated products. At the same time, it has been shown in [10] that over Al_2O_3 the 1-tetralone methylation at C-2 position and oxygen-elimination (reduction) are consecutive reactions. Therefore, the selectivity towards 2-methyl-1-tetralone (intermediate) was observed to decrease when the reaction conversion increased with temperature, while the selectivity towards 2-methyl-3,4-dihydronaphthalene increased (Table 1). In principle, variation of reaction temperature and amount of a basic modificator in alumina allow to change significantly ration of the final products. Nevertheless, reaction selectivity towards 2-methyl-1-tetralone was not observed to be higher than 74%.

Iron oxide supported on Al_2O_3 also demonstrated low selectivity towards 2-methyl-1-tetralone. The re-
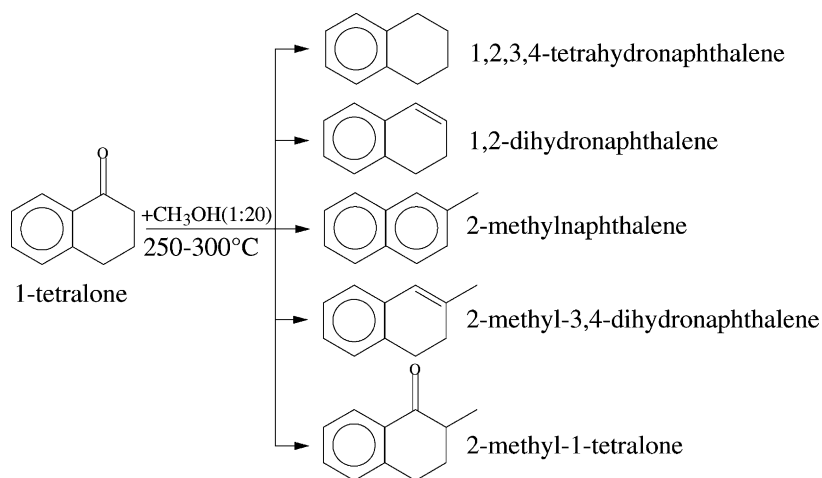
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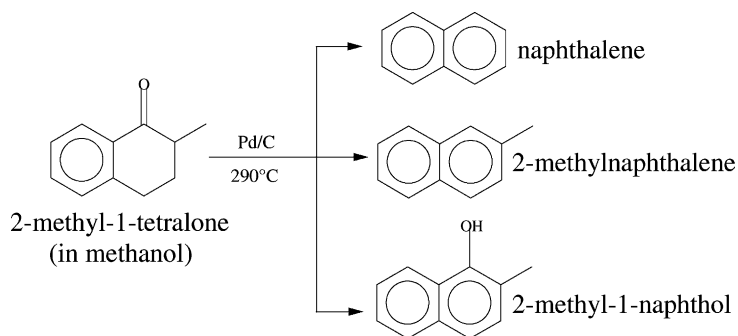
Scheme 3.

sult confirmed very strong influence of support acidity on the catalytic properties.

The best result in 1-tetralone methylation was obtained over the iron oxide catalyst modified by chromium, silicon and potassium ions (see Table 1). In this case 2-methyl-1-tetralone was found to be the main product of the reaction. High selectivity (>90%) at 88% conversion of 1-tetralone was attained at 270 °C. No catalyst deactivation was observed during the long-term (∼24 h) catalytic test.

3.2. Dehydrogenation of 2-methyl-1-tetralone and 1-tetralone

The reactions were investigated over Pd supported catalysts in the temperature range from 250 to 350 °C. The main products of 2-methyl-1-tetralone dehydrogenation are presented in the Scheme 3.

Very high selectivity (∼94%) towards 2-methyl-1-naphthol at 80% conversion of 2-methyl-1-tetralone was obtained over Pd supported on activated carbon.

During the investigation, it was found that 2-methyl-1-tetralone and 1-tetralone, which have the similar chemical structures, behave in the same manner in the reaction of dehydrogenation. That is why it was decided to use 1-tetralone instead of 2-methyl-1-tetralone for further catalytic tests and optimisation of the reaction conditions.

The results obtained in 1-tetralone dehydrogenation are presented in Table 2.

During the tests, it was found that the catalyst support strongly influences the reaction mechanism. Very high selectivity towards 1-naphthol (97–99%) was achieved over Pd supported on activated carbon

at 270–290 °C. Selectivity decreased with temperature. No traces of 1-naphthol were observed over Pd supported on Al$_2$O$_3$. In this case, the reaction of aromatisation proceeds simultaneously with elimination of oxygen atom. The main product of 1-tetralone conversion over Pd supported on Al$_2$O$_3$ was found to be naphthalene.

Distribution of the reaction products did not depend on a diluent used. As seen from Table 2, the very close results were obtained under the same conditions for the different solvents (heptane, benzene, methanol). No catalyst deactivation was observed during the long-term (∼8 h) catalytic tests.

3.3. One-step 1-naphthol synthesis

The results obtained during the investigation of 1-tetralone methylation and 2-methyl-1-tetralone dehydrogenation indicate that the reactions proceed over appropriate catalysts with high yields of the desired products. It is also important that the reactions proceed under the same conditions. In both cases, the reaction temperatures were in the range from 270 to 290 °C. Methanol was used as a methylating agent and/or a diluent of the substrates.

On the base of these results, we can propose carrying out the methylation and dehydrogenation stages of 1-tetralone without separation and purification of the intermediates. The catalytic reactors used for different stages can be connected in line. It is also possible to explore a single reactor with a two-layer or mixed catalytic bed (Fig. 2).

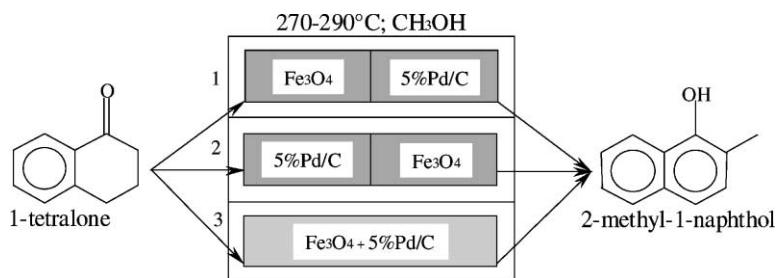In order to check this approach, one of the possible reactor configurations was tested. Synthesis of

Fig. 2. The possible compositions of the catalytic bed for 2-methyl-1-naphthol production.

Table 3
Methylation and dehydrogenation of 1-tetralone in the reactor with two-layered catalytic bed ($T = 280\,^{\circ}C$; $F_0 = 1.4 \times 10^{-2}\,mol\,h^{-1}$; diluent—methanol)

Catalysts	Conversion of 1-tetralone (%)	Yield of 2-methyl-1-naphthol (%)	Yield of 1-naphthol (%)	Yield of 2-methyl-1-tetralone (%)	Selectivity to useful products (%)
First layer—Fe$_3$O$_4$(SiCrK) (10 g) + second layer—5%Pd/C (10 g)	98	66	12	3	83

2-methyl-1-naphthol was carried out in the reactor with two-layer catalytic bed (1). The first layer comprised the iron oxide catalyst modified by chromium, silicon and potassium, the second one—Pd (5 wt.%) supported on activated carbon. The obtained results are presented in Table 3.

As seen from Table 3, very high conversion of 1-tetralone and high yield of the desired product was reached using two-layered catalytic bed without intervening reaction mixture separation. It is also important to notice that 1-naphthol and 2-methyl-1-tetralone detected among the reaction products are the intermediates of 2-methyl-1-naphthol synthesis. As it was demonstrated above, they could be successfully converted to 2-methyl-1-naphthol over the used catalysts. The presence of these compounds in the product mixture indicates that the used reaction conditions (residence time, reaction temperature, catalyst loading) should be optimised to increase yield of the desired product. At the same time, the obtained results convincingly demonstrate the possibility of one-step vapour-phase synthesis of 2-methyl-1-naphthol from 1-tetralone.

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