

## Solvent-free liquid-phase autoxidation of monoterpenes catalyzed by sol–gel Co/SiO<sub>2</sub>

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### Abstract

Oxidation of limonene, 3-carene,  $\alpha$ -pinene and  $\beta$ -pinene with dioxygen promoted by heterogeneous sol–gel Co/SiO<sub>2</sub> catalysts has been performed under solvent-free conditions. Limonene and  $\alpha$ -pinene give both epoxidation and allylic oxidation products, with chemoselectivities for the latter being 50–60% at a 40% substrate conversion. On the other hand, oxidation of  $\beta$ -pinene leads essentially to allylic products, i.e., highly valuable pinocarveol, pinocarpone, myrtenol and myrtenal. Good combined selectivities of up to 88% at ca. 40% conversion have been achieved. The activity of the Co/SiO<sub>2</sub> catalysts is strongly influenced by the temperature of their thermal treatment. No cobalt leaching occurs under the reaction conditions and the catalysts can be recovered and reused several times.

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### 1. Introduction

The application of conventional homogeneous systems in metal complex catalysis is frequently complicated by serious technological and environmental problems associated with catalyst recovering and large amounts of effluents. The use of solid materials in catalytic oxidations in the liquid-phase has recently been extensively investigated because of their easy recovery and the possibility of regeneration which results in a reduction of the environmental impact [1–3]. One of the approaches for developing heterogeneous catalysts is to incorporate redox metal ions into the lattice of molecular sieves, such as zeolites, aluminophosphates and silicalites [1]. Glasses doped with transition metals also form a class of materials important as catalysts [4–7]. Solids with highly dispersed active components can be obtained by a sol–gel method that allows a nanostructural control of ceramics through process variables. Incorporation of small amounts of different components in the ceramic matrix us-

ing this method offers nanocomposites with a high surface area and high homogeneity of the chemical composition. Sol–gel techniques usually can afford much higher levels of incorporation than conventional impregnation methods.

Monoterpenes are widely distributed in nature and are very important for flavor and fragrance industry. Terpenic aldehydes, alcohols and esters often show valuable organoleptic properties and form the largest group of modern fragrance ingredients [8–11]. We have previously studied catalytic oxidations of some monoterpenes using both dioxygen and hydrogen peroxide as final oxidants [12–19]. Limonene and  $\beta$ -pinene were selectively oxidized into allylic acetates in PdCl<sub>2</sub>(cat)/CuCl<sub>2</sub>(cat)/O<sub>2</sub> and Pd(OAc)<sub>2</sub>(cat)/H<sub>2</sub>O<sub>2</sub> systems, respectively [12,13,18]. A conventional Wacker catalyst (PdCl<sub>2</sub>/CuCl<sub>2</sub>) promoted oxidative cyclization of myrcene giving new acetates with a cyclopentane skeleton [15]. Oxidation of camphene with hydrogen peroxide catalyzed by Pd(OAc)<sub>2</sub> resulted in glycol derivatives [13], whereas a Pd(II)/NO<sub>n</sub><sup>-</sup> ( $n = 2, 3$ ) catalytic system promoted an aerobic tandem oxidative coupling/oxidation of this substrate [14,16,17]. Recently, we have reported a CoCl<sub>2</sub> catalyzed autoxidation of limonene,  $\alpha$ -pinene and  $\beta$ -pinene in acetic acid and acetonitrile so-

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lutions [19]. In acetic acid, the reactions usually gave a complex mixture of oxygenated products, while in acetonitrile, good combined chemoselectivities for epoxidation and/or allylic oxidation products were obtained for all substrates studied. The aim of the present work is to develop a heterogeneous version of this catalyst.

Autoxidation of alkylbenzenes and alkanes by cobalt catalyzed homolytic processes has been extensively studied because of their industrial importance [20–23]. Surprisingly, autoxidation of alkenes in the presence of cobalt complexes has attracted much less attention [20,21,24–26]. In these reactions a free radical chain mechanism is usually suggested and a competition between the abstraction of the allylic hydrogen to give allylic oxidation products and the addition of the alkylperoxy radical to the double bond resulting in epoxide products is expected [20]. Some reports on the cobalt catalyzed homogeneous autoxidation of a number of monoterpenes including limonene [19,27], 3-carene [28,33],  $\alpha$ -pinene [19,27–35] and  $\beta$ -pinene [19,27] have previously been published. Oxidation of  $\alpha$ -pinene has gained more attention because, one of its oxidation product, i.e., verbenone, is used for the synthesis of taxol, an important therapeutic agent [36,37]. In the autoxidation of  $\alpha$ -pinene, some cobalt containing solid materials, such as zeolites and activated carbons, have been also applied as catalysts [38,39].

We wish to report here the use of sol–gel Co/SiO<sub>2</sub> as active and recyclable heterogeneous catalysts for the oxidation of limonene, 3-carene,  $\alpha$ -pinene and  $\beta$ -pinene with dioxygen under solvent-free conditions, which offers important technological and environmental advantages. Highly selective oxidation of  $\beta$ -pinene into valuable allylic derivatives has been developed.

## 2. Experimental

All reagents were purchased from commercial sources and used as received, unless otherwise indicated. Monoterpenes were distilled before use.

### 2.1. Catalyst preparation

The Co/SiO<sub>2</sub> materials were prepared by a sol–gel method using tetraethoxysilane (TEOS) and Co(NO<sub>3</sub>)<sub>2</sub> as precursors. The cobalt content was 5 mol%. The sol was obtained from a TEOS/ethanol/water mixture in a 1/3/10 molar ratio with the addition of HCl and HF (up to pH 2.0) as catalysts. The samples were prepared in a monolithic shape, dried at 110 °C for 48 h and thermally treated for 2 h at 700, 900 and 1100 °C in air.

### 2.2. Catalyst characterization

The materials were characterized by X-ray diffraction (XRD) using a Rigaku Geigerflex-3034 diffractometer with CuK $\alpha$  radiation. Samples were previously dried and pul-

verized. The pore characteristics of the catalysts and their BET surface areas were analyzed using a nitrogen adsorption on an Autosorb-Quantachrome NOVA 1200 equipment. Samples were outgassed for 2 h at 300 °C before the analysis. FT-IR spectra were recorded on a Bomem 102 Fourier-transform spectrometer.

### 2.3. Catalytic oxidation experiments

Reactions were carried out in a glass reactor equipped with a magnetic stirrer, a sampling system and connected to a gas burette to monitor the oxygen uptake. In a typical run, a mixture of monoterpene (18 mmol) and Co/SiO<sub>2</sub> (0.125 g, 5 wt.%) was intensively stirred at 60 °C and oxygen pressure of 0.1 MPa for 24 h. Reactions were followed by measuring the dioxygen uptake and by gas chromatography (GC) using dodecane as an internal standard (Shimadzu 17 instrument, Carbowax 20 M capillary column). At appropriate time intervals, stirring was stopped and after quick catalyst settling aliquots were taken, diluted 20-fold with acetonitrile and analyzed by GC. The GC mass balance typically made up ca. 95% based on the substrate charged except 3-carene. The difference was attributed to the formation of oligomers, which were not GC determinable and estimated semiquantitatively. The oligomers adsorbed on the catalyst surface were determined from the difference in the catalyst weight before and after use. The structure of the products were confirmed by GC–MS (Hewlett-Packard MSD 5890/Series II, 70 eV) by comparison with the authentic samples. After the reaction, the catalyst was filtered off, washed with acetonitrile and reused. To control the leaching, the catalyst was filtered off at the reaction temperature after 7 h and the reaction was kept running in the solution.

## 3. Results and discussion

### 3.1. Characterization of the catalysts

XRD patterns of the samples doped with cobalt indicate that a treatment at 700–1100 °C causes a complete decomposition of the cobalt precursor, Co(NO<sub>3</sub>)<sub>2</sub>, which has been also confirmed by a FTIR characterization. XRD shows that the SiO<sub>2</sub> matrix is essentially amorphous in all samples studied. Only after the treatment at 1100 °C, the amorphous matrix partially crystallizes, with cristobalite and tridimite phases appearing in minor amounts (<3%). Samples treated at 700 and 900 °C exhibit the patterns attributed to a Co<sub>3</sub>O<sub>4</sub> phase, while the samples treated at 1100 °C contain cobalt mainly as a Co<sub>2</sub>SiO<sub>4</sub> phase.

Surface area, pore size and total pore volume of the samples treated at different temperatures are given in Table 1. It can be seen that the sample treated at 700 °C shows maximum values for all these parameters. After drying at 110 °C, the samples are impregnated with organic compounds, which are removed at 700 °C since the samples lost weight. Once

Table 1  
Structural characteristics obtained by BET analysis for 5 mol% Co/SiO<sub>2</sub> treated at different temperatures

Temperature (°C)	Surface area (m <sup>2</sup> /g)	Pore size (Å)	Pore volume (×10 <sup>-3</sup> cm <sup>3</sup> /g)
700	220	35	391
900	153	29	227
1100	37	17	125

the organics are eliminated from the network, the increase of the free volume contributes to the increase in the porosity and in the solid-pore interface. Above 700 °C, a densification of the material begins and the pores gradually collapse causing a high shrinkage in the materials. This leads to the decrease in the surface area and in the average size and total volume of the pores. Samples treated at 700 and 900 °C show the surface area of 220 and 153 m<sup>2</sup>/g, respectively, while a treatment at 1100 °C significantly decreases the surface area to 37 m<sup>2</sup>/g due to the strong densification process.

The samples treated at 700 and 900 °C present a type IV adsorption isotherm according to the BDDT classification, which is characteristic of mesoporous materials. Composites dried at 110 °C without additional thermal treatment show characteristics of a non-porous material, i.e., a type II isotherm, due to the pore obstruction by organic compounds. The treatment at 1100 °C drastically decreases the total porosity of the sample and reduces the adsorption. During the gel to glass conversion the dried gel becomes progressively more highly cross-linked while its free volume decreases by structural relaxation and its pore surface area is decreased by viscous sintering.

### 3.2. Catalytic studies

Oxidation of limonene (**1**), 3-carene (**2**), α-pinene (**3**) and β-pinene (**4**) was performed under non-solvent conditions. In all experiments, Co/SiO<sub>2</sub> composites alone were applied as catalysts without the addition of bromide ions, which are usually used as auxiliary hydrogen abstraction agents in cobalt catalyzed oxidation processes. The results are presented in Tables 2–5. Sol-gel Co/SiO<sub>2</sub> samples ef-

Table 3  
Oxidation of 3-carene (**2**) catalyzed by Co/SiO<sub>2</sub><sup>a</sup>

Run	Catalyst <sup>b</sup>	Conversion (%)	Product selectivity (%)		S <sub>allyl</sub> <sup>c</sup> (%)
			<b>8</b>	<b>9</b>	
1	Co/SiO <sub>2</sub> /900 °C	66	9	11	20
2	Co/SiO <sub>2</sub> /1100 °C	60	13	10	23

<sup>a</sup> Conditions: Co/SiO<sub>2</sub> (5 wt.%), 60 °C, 1 MPa (O<sub>2</sub>), reaction time 24 h. Conversion and selectivity were determined by GC.

<sup>b</sup> Temperature of catalyst treatment.

<sup>c</sup> Selectivity for allylic oxidation products (**8** and **9**).

fectively catalyze the autoxidation of all these substrates, with the materials treated at 700 °C (Co/SiO<sub>2</sub>/700 °C) and 900 °C (Co/SiO<sub>2</sub>/900 °C) being much more active than those treated at 1100 °C (Co/SiO<sub>2</sub>/1100 °C). Although, Co/SiO<sub>2</sub>/700 °C composites show catalytic properties similar to those treated at 900 °C, their application in neat liquid substrates is slightly complicated by rather slow catalyst settling. Selectivities for corresponding products obtained with heterogeneous catalysts are comparable with those reported in our previous work for homogeneous systems [19]. Limonene and α-pinene produce a wide variety of oxygenated derivatives, with the relative amounts of allylic oxidation products being of near 50% based on the reacted substrate. β-Pinene gives almost exclusively allylic oxidation products in near 90% combined selectivity, which should be considered rather high for the reactions involving free radicals.

Limonene forms three main products: limonene oxide (**5**) (*cis/trans* ≈ 1/1), carvone (**6**) and carveol (**7**) (≈80% *cis*), each in 20–30% selectivity (Scheme 1, Table 2). Approximately 40% conversions are achieved for 24 h at 60 °C with Co/SiO<sub>2</sub>/700 °C and Co/SiO<sub>2</sub>/900 °C. After 40–50% substrate conversion, the reaction rates and product selectivities significantly decrease for all substrates due to the further oxidation of primarily formed compounds. The *endo*-cyclic double bond of limonene is much more sensitive to epoxidation: epoxide resulting from the oxidation of the terminal *exo* double bond is detected in three to five times lower amounts than epoxide (**5**).

Table 2  
Oxidation of limonene (**1**) catalyzed by Co/SiO<sub>2</sub><sup>a</sup>

Run	Catalyst <sup>b</sup>	Conversion (%)	Product selectivity (%)		S <sub>allyl</sub> <sup>c</sup> (%)	S <sub>epox</sub> <sup>d</sup> (%)	
			Epoxidation <sup>e</sup>	Allylic oxidation			
				<b>6</b>			<b>7</b>
1	Co/SiO <sub>2</sub> /700 °C	40	30	20	24	44	30
2	Co/SiO <sub>2</sub> /900 °C	41	24	24	28	52	24
3	Co/SiO <sub>2</sub> /1100 °C	20	26	22	25	47	26

<sup>a</sup> Conditions: Co/SiO<sub>2</sub> (5 wt.%), 60 °C, 1 MPa (O<sub>2</sub>), reaction time 24 h. Conversion and selectivity were determined by GC.

<sup>b</sup> Temperature of catalyst treatment.

<sup>c</sup> Selectivity for allylic oxidation products (**6** and **7**).

<sup>d</sup> Selectivity for epoxidation products.

<sup>e</sup> Mainly *endo*-epoxide (**5**), along with small amounts of *exo*-epoxide (*endo/exo* ≈ 4/1).

Table 4  
Oxidation of  $\alpha$ -pinene (**3**) catalyzed by Co/SiO<sub>2</sub><sup>a</sup>

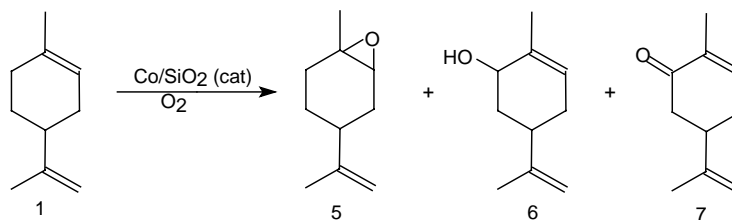
Run	Catalyst <sup>b</sup>	Conversion (%)	Product selectivity (%)				S <sub>allyl</sub> <sup>c</sup> (%)	S <sub>epox</sub> <sup>d</sup> (%)	
			Epoxidation		Allylic oxidation				
			<b>10</b>	<b>11</b>	<b>12</b>	<b>13</b>			<b>14</b>
1	Co/SiO <sub>2</sub> /900 °C	40		5	9	34	26	60	14
2	Co/SiO <sub>2</sub> /1100 °C	3	18		17	25	10	35	35

<sup>a</sup> Conditions: Co/SiO<sub>2</sub> (5 wt.%), 60 °C, 1 MPa (O<sub>2</sub>), reaction time 24 h. Conversion and selectivity were determined by GC.

<sup>b</sup> Temperature of catalyst treatment.

<sup>c</sup> Selectivity for allylic oxidation products (**13** and **14**).

<sup>d</sup> Selectivity for epoxidation products (**10–12**).



Scheme 1.

Table 5  
Oxidation of  $\beta$ -pinene (**4**) catalyzed by Co/SiO<sub>2</sub><sup>a</sup>

Run	Catalyst <sup>b</sup>	Conversion (%)	Product selectivity (%)				S <sub>allyl</sub> <sup>c</sup> (%)
			<b>15</b>	<b>16</b>	<b>17</b>	<b>18</b>	
1	Co/SiO <sub>2</sub> /700 °C	32	11	23	23	30	87
2	Co/SiO <sub>2</sub> /900 °C	36	10	22	24	32	88
3	Co/SiO <sub>2</sub> /1100 °C	7	23	25	23	22	93
4 <sup>d</sup>	Co/SiO <sub>2</sub> /900 °C	3.5	15	20	22	26	83

<sup>a</sup> Conditions: Co/SiO<sub>2</sub> (5 wt.%), 60 °C, 1 MPa (O<sub>2</sub>), reaction time 24 h. Conversion and selectivity were determined by GC.

<sup>b</sup> Temperature of catalyst treatment.

<sup>c</sup> Selectivity for allylic oxidation products (**15–18**).

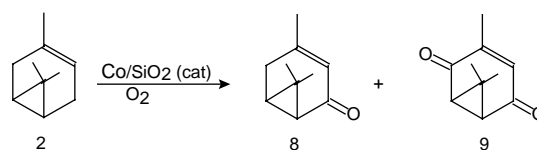
<sup>d</sup> The catalyst was filtered off after 7 h and the filtrate was allowed to react further.

Oxidation of 3-carene (**2**) gives a complex mixture of various products with low selectivity being observed for any specific compound. Two allylic oxidation products, i.e., 3-carene-5-one (**8**) and 3-carene-2,5-dione (**9**), have been detected, each in ca. 10% selectivity (Scheme 2, Table 3). No epoxide or epoxide-derived products have been identified in the reaction solutions, which has also been found in earlier studies and explained by comparing the stability of corresponding radical intermediates [28]. In the oxidation of 3-carene under the conditions used, oligomers account for ca. 20% of a mass balance. At 60 °C, even in the absence of cobalt catalysts, 3-carene undergoes a rapid conversion giving numerous unidentified products and non-GC determinable oligomers (60% conversion for 24 h under O<sub>2</sub>).

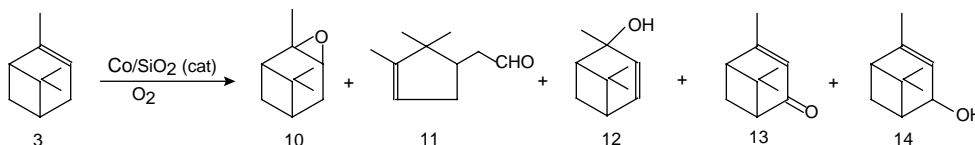
On the other hand, blank reactions with neat limonene,  $\alpha$ -pinene and  $\beta$ -pinene in which no catalyst was added showed virtually no activity (<2% conversion for 24 h at 60 °C). Oxidation of  $\alpha$ -pinene catalyzed by Co/SiO<sub>2</sub>/900 °C results mainly in verbenone (**13**) (34%) and *trans*-verbenol (**14**) (26%), along with smaller amounts of campholene

aldehyde (**11**) (5%) and 3-pinen-2-ol (**12**) (9%) (Scheme 3, Table 4). A substrate conversion of 40% has been achieved with Co/SiO<sub>2</sub>/900 °C for 24 h, while Co/SiO<sub>2</sub>/1100 °C exhibits only slight activity (3% conversion). Products (**11**) and (**12**) more likely result from the skeletal rearrangement of  $\alpha$ -pinene oxide (**10**) under the reaction conditions [34], thus they are referred in Table 4 as epoxidation products. Epoxide (**10**) itself has been detected in appreciable amounts only in the blank reaction and with the Co/SiO<sub>2</sub>/1100 °C catalyst.

We have observed a strong effect of monoterpene structure on the product nature studying the oxidation of  $\beta$ -pinene (**4**),



Scheme 2.



Scheme 3.

which gives almost exclusively allylic oxidation products. High combined selectivity of ca. 90% for *trans*-pinocarveol (15), pinocarvone (16), myrtenal (17) and myrtenol (18) has been achieved, with neither epoxide nor corresponding glycol derivatives being detected in the reaction mixtures (Scheme 4, Table 5). In our previous study on the homogeneous autoxidation of monoterpenes catalyzed by CoCl<sub>2</sub> [19],  $\beta$ -pinene also exhibited a strong preference compared to  $\alpha$ -pinene for allylic oxidation over epoxidation. That observation was explained by different reactivity of the allylic hydrogens in the molecules of these monoterpenes toward the abstraction.

A 30–40% conversion of  $\beta$ -pinene has been achieved for 24 h with Co/SiO<sub>2</sub>/700 °C and Co/SiO<sub>2</sub>/900 °C catalysts, after which the reaction rate and selectivity significantly decrease. As with other substrates, Co/SiO<sub>2</sub>/1100 °C shows much lower activity producing only a 7.5% conversion for 24 h. It should be mentioned, that differently to other monoterpenes oxidation of  $\beta$ -pinene shows an appreciable induction period of ca. 5 h. To control leaching of the active metal, the Co/SiO<sub>2</sub>/900 °C catalyst was filtered off at the reaction temperature after 7 h of using and the filtrate was allowed to react further (Table 3, run 4). No additional conversion of  $\beta$ -pinene was observed after catalyst removing, which supports a heterogeneous catalysis. Thus, the reaction solution contains no significant amounts of the dissolved cobalt species and the cobalt ions immobilized in the solid matrix are responsible for the substrate oxidation. In run 2 after the reaction, the catalyst was filtered off, washed with acetonitrile and used repeatedly (three times) with virtually no loss of activity.

We have found that a catalytic behavior of the sol–gel Co/SiO<sub>2</sub> materials strongly depends on the temperature of their treatment. As shown by the results of the sample characterization, the treatment temperature determines the nature of the cobalt phase present in the matrix and the extent of the densification of the matrix itself. The samples treated at 700 and 900 °C showed the best activity in the autoxidation of monoterpenes. Much poorer catalytic activity of the Co/SiO<sub>2</sub>/1100 °C composites can be attributed to the densification of the silica matrix, to the decrease in the surface

area and to the entrapment of the cobalt species occurring at high temperatures as shown by the results of the catalyst characterization. In addition, the nature of the active cobalt phase seems also to be highly important and should be considered to explain the results obtained. XRD patterns show the intense crystallization of cobalt as Co<sub>3</sub>O<sub>4</sub> in the Co/SiO<sub>2</sub>/700 °C and Co/SiO<sub>2</sub>/900 °C samples, while those treated at 1100 °C contain cobalt mainly as Co<sub>2</sub>SiO<sub>4</sub>. It is well-known that cobalt catalyzed free radical autoxidation processes involve Co(II) and Co(III) valence changes [20]. Thus, the ease of interconversion of Co(II) and Co(III) ions should be critical for the activity of the catalyst and expectedly should be strongly dependent on the particular accommodation of cobalt in the solid matrix.

#### 4. Conclusions

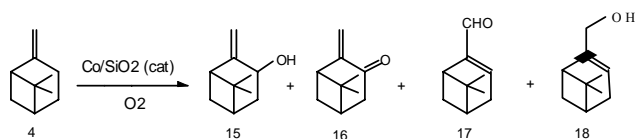
The sol–gel process was found to be a promising method to immobilize a homogeneous cobalt catalyst for the liquid-phase autoxidation of renewable and inexpensive natural monoterpenes. The Co/SiO<sub>2</sub>/700 °C and Co/SiO<sub>2</sub>/900 °C materials showed a reasonable catalytic activity and selectivity under solvent-free conditions and proved to be recyclable. The selective heterogeneous oxidation of  $\beta$ -pinene resulting in highly valuable allylic oxygenated derivatives, i.e., pinocarveol, pinocarvone, myrtenol and myrtenal, has been developed. Limonene and  $\alpha$ -pinene give both epoxidation and allylic oxidation products, with chemoselectivities for the latter being 50–60%. No leaching of active cobalt species occurs under the reaction conditions and the catalysts can be recovered and reused several times.

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Scheme 4.

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