Sulphated Zirconia in the Alkylation of *ortho*-Cresol by Camphene

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Abstract

An influence of the synthesis conditions upon the direction of *o*-cresol alkylation conditions with camphene in the presence of sulphated zirconia was investigated. There were O- and C-alkylation products obtained with a different structure of terpene substituent. It is demonstrated that the presence of sulphated zirconia results in the formation of 4-isobornylphenol, 4-isocamphylphenol and *para*-alkylated phenol with the methyl groups at positions 1, 4, 7 in the terpene moiety. The catalysis with sulphated zirconia allows obtaining *para*-alkylated 2-methylphenol with the isobornyl structure of terpene substituent, with a yield of 58 %.

Key words: sulphated zirconia, alkylation, *ortho*-cresol, camphene

INTRODUCTION

The alkylation of phenols is an industrially important process for the production of alkyl phenols used as antioxidants, stabilizers and precursors for obtaining useful products [1]. The alkylation of phenols is studied in sufficient detail. Of the greatest practical interest are mono- and dialkylphenols derived from phenolic compounds resulting from the alkylation of various alkylating agents: olefins, alcohols, ethers. Usually, for this type of reaction there are used acidic catalysts used such as $AlCl_3$, H_2SO_4, HF, and BF_3. Using a homogeneous catalyst is associated with a number of problems such as the corrosion of equipment, the need to provide safe conditions for the processes, the recycling of spent catalysts, *etc.* In addition, homogeneous catalysts cannot be reused. In this regard, at the present time increasing interest is observed in the studying the heterogeneous catalysis of alkylation.

Owing to the thermal stability, recyclability and high acidity, sulphated zirconia is of great interest of researchers. There are Lewis, Brцnsted and mixed acidic sites, formed as a result of sulphation on the surface of sulphated zirconia [2]. There is a number of examples concerning the application of this catalyst in the alkylation processes presented in the literature [3–8]. The present work was performed in order to investigate the activity of sulphated zirconia in the reaction of *o*-cresol alkylation with camphene.

RESULTS AND DISCUSSION

Earlier, we investigated the alkylation of resorcinol by camphene using sulphated zirconia [9]. It should be noted that in this case, the mono- and dialkylated resorcinols have the isobornyl structure of terpene substituent. The terpene moiety has chiral centers; therefore in
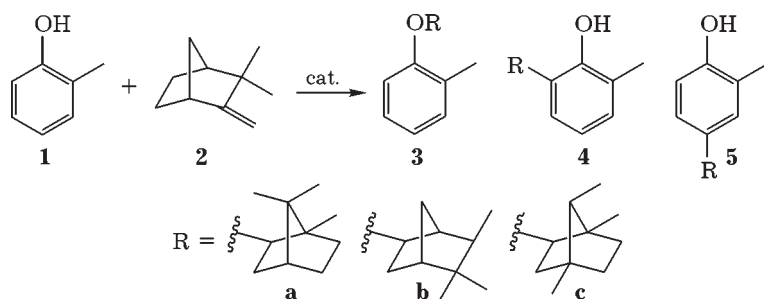
Scheme 1.

the case of resorcinol dialkylation the product composition is complicated to a significant extent not only by regioisomers but also by diastereomers. In this regard, further we chose *o*-cresol for testing of the catalysts under investigation.

The literature describes the alkylation of *o*-cresol by camphene on wide-porous β-zeolite [10]. As the result of this process, in the solvent system dichloromethane − benzene there was isobornyl cresol ether **3a** as the major product formed with 29 % yield, whereas in the course of the reaction in dichloromethane there is *para*-substituted cresol with 1, 4, 7 positions of the methyl groups in the terpene substituent **5c** (33 % yield). The interaction between *o*-cresol and camphene in the presence of aluminum cresolate at 155 °C results in the formation of equal amounts of 2-methyl-6-isobornylphenol **4a** and 2-methyl-6-isocamphylphenol **4b** (42 %) [11].

We have studied the effect of different conditions on the course of the process of *o*-cresol alkylation with camphene in the presence of 5 % sulphated zirconia calcined at 450 °C (5 % ZrO_2/SO_4^{2-} (450)). In the presence of SO_4^{2-}/ZrO_2 there were formed mainly the products of *para*-substitution. In this case there occurred terpene rearrangements to form isocamphylphenols and the products with 1, 4, 7 positioned methyl groups in the terpene moiety (Scheme 1). It is known that in the presence of acidic catalysts ($HClO_4$, H_2SO_4, polyphosphoric acid), there occurs a cascade of skeletal rearrangements of bicyclic monoterpene camphene to form terpenophenols with different structural types of the terpene fragment [11, 12]. Judging by the products, similar same could occur also in the case of catalysis by sulphated zirconia.

The results of studying the effect of reaction temperature on the *o*-cresol conversion level and on alkylation selectivity are presented in Table 1.

Increasing the reaction temperature from 60 to 120 °C resulted in an increase in the level of *o*-cresol conversion. However, already at the temperature equal to 120 °CC the selectivity of the process decreased with respect to 4-isobornyl-2-methylphenol (**5a**). Under these conditions, products **5a** and **5c** are formed in almost equal amounts. Further increasing the temperature did not result in an increase in the conversion level of starting materials. This can probably be explained by a deactivation of the active centres on the catalyst surface. From this standpoint, the optimum temperature is equal to 80 °C.

TABLE 1

Effect of temperature on the conversion of *o*-cresol and the selectivity of *o*-cresol alkylation by camphene (process conditions: catalyst 5 % ZrO_2/SO_4^{2-} calcined at 450 °C; molar ratio *o*-cresol/camphene = 1 : 1; 6 h)

Temperature, °C	Conversion level, %	Selectivity level, %				
		3a	4a	5a	5b	5c
140	71	−	18	27	13	42
120	77	−	12	36	10	42
80	71	−	15	40	18	27
60	55	9	10	45	18	18

Note. Dash − absence.

TABLE 2

Effect of alkylation time on the conversion level alkylation selectivity (process conditions: catalyst 5 % ZrO_2/SO_4^{2-} calcined at 450 °C; molar ratio *o*-cresol/camphene = 1 : 1; 80 °C)

Time, h	Conversion level, %	Selectivity level, %				
		3a	**4a**	**5a**	**5b**	**5c**
1	52	42	6	17	13	22
3	63	29	8	34	14	15
6	71	–	15	40	18	27
9	79	–	24	38	14	24

Note. Dash – absence.

An effect was investigated concerning the duration of the reaction mixture interaction on the values of conversion and selectivity level. It has been established that increasing the interaction time for the reaction mixture causes increasing the level of conversion with changing the ratio between the reaction products. However, with the duration of heating being over 6 h the conversion level exhibits slowing down the growth and changing the ratio between the reaction products is almost absent (Table 2). To all appearance, in this case also a deactivation of the strongest acidic sites takes place, which causes the reaction rate of the initial substances to decrease.

The *o*-cresol/camphene molar ratio was varied within the range of 1 : (0.5–2). With increasing the content of cresol in the reaction mixture the alkylation proceeded with 100 % conversion level with respect to camphene, whereas decreasing the yield of the products with non-isobornyl structure of the terpene substituent occurred and increasing the yield of 5a was observed (Fig. 1). The excess of camphene promoted the rearrangement to occur and the

formation of compounds **5a** and alkylated cresol **5c** in the reaction mixture as the main products. Also, the excess of camphene resulted in increasing the formation of cresol **4a**.

We investigated the yield of the reaction products depending on the amount of catalyst 5 % ZrO_2/SO_4^{2-} (450) at 80 °C, at the molar ratio *o*-cresol/camphene = 2 : 1 (Table 3). It has been found that increasing the amount of catalyst causes the ether formation to decreases and promotes the C-alkylation predominantly to occur. It should be noted that changing the amount of the catalyst affects to a considerable extent only the yield of products **3a** and **5a**. At the same time, introducing the catalyst in an amount exceeding 50 mass % has no significant effect on the yield of 4-isobornyl-2-methylphenol **5a**.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra of the compounds obtained were registered using a Bruker Avance II 300 NMR spectrometer 300 and 75 MHz, re-
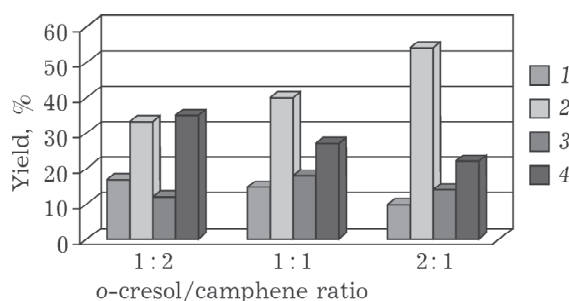

Fig. 1. Effect of *o*-cresol/camphene molar ratio on the yields of alkylation products: **4a** (*1*), **4b** (*2*), **5b** (*3*), **5c** (*4*).

TABLE 3

Effect of the catalyst amount on the yield of alkylation products, %

Amount of catalyst, mass %	**3a**	**4a**	**5a**	**5b**	**5c**
10	31	14	39	–	16
30	12	16	44	11	17
50	–	12	58	8	22
70	–	18	56	7	19
100	–	13	54	11	22

Note. Dash – absence.

spectively) in CDCl$_3$ at a room temperature. As the internal standard we used the signals of chloroform (δ_H = 7.26 ppm, δ_C = 76.90 ppm). The assignment of signals was performed using the ^{13}C NMR spectra registered in a JMOD mode.

The purity control of source cresol, camphene and the analysis of volatile products of the reactions were monitored using GLC with the help of a Shimadzu GC-2010AF chromatograph equipped with a flame ionization detector (carrier gas being helium), a HP-1 capillary column (Agilent, 60 m × 0.25 mm × 0.25 μm, temperature 100−240 °C, heating rate 6 °C/min).

Catalyst ZrO$_2$/SO$_4^{2-}$ was prepared by means of the procedure described in [5], *via* the reaction between an aqueous solution of ammonia (25 %) and ZrOCl$_2$ · 8H$_2$O at a room temperature at pH 8. A precipitate obtained was filtered, washed with distilled water to obtain a negative response for chloride ions (reaction with AgNO$_3$) and dried at 120 °C for 24 h.

The resulting zirconium hydroxide was impregnated with an appropriate amount of 1 M (NH$_4$)$_2$SO$_4$ solution, and then it was dried at 120 °C during 24 h and calcined at a temperature of 450 °C. The crystallographic phase composition of the catalyst was determined by means of X-ray diffractometry with the use of a Shimadzu XRD-6000 diffractometer (CuK$_\alpha$ radiation). Scanning was performed within the range of 2θ = 10−80 deg. The specific surface area and porosity of the catalyst was measured by means of N$_2$ physical sorption employing an ASAP 2400 V3.07 unit. In order to calculate the surface area we used a standard multi-point BET method.

The powder X-ray diffraction pattern of ZrO$_2$/SO$_4^{2-}$ calcined at 450 °C demonstrated the presence of the only tetragonal phase of zirconium dioxide. The specific surface area of the catalyst was equal to 137 m^2/g, the pore volume amounting to 0.145 mL/g, the average pore size being of 42 Å. The characteristics of the catalyst are in a good agreement with data available from the literature [5].

To a two-neck flask equipped with a thermometer and a backflow condenser, were placed a weighed sample portion of *o*-cresol (1.00 g, 9 mmol) and of camphene (1.24 g, 9 mmol) and the catalyst was added. In the case of changing the *o*-cresol/camphene ratio weighed portion of the component used in ex-

cess was increased in proportion. The reaction was carried out at the temperature values ranging from 80 to 140 °C with continuous stirring (GLC monitoring). After completing the synthesis, the reaction mixture was dissolved in diethyl ether and filtered to remove the catalyst. The resulting solution was evaporated on a rotary evaporator. The separation of the reaction products was performed using a column chromatography technique (filling be means of a "wet" method) on Alfa Aesar 70/230μ silica gel, with the elution of substances using petroleum ether−diethyl ether solvent system.

The spectral characteristics of the compounds correspond to the literature data [10].

CONCLUSION

Thus, we investigated the alkylation of *o*-cresol with camphene in the presence of sulphated zirconia. It has been found that 5 % ZrO$_2$/SO$_4^{2-}$ calcined at 450 °C, represents an active *para*-orienting catalyst of *o*-cresol alkylation by camphene. An influence of the alkylation conditions on the direction of the process was studied. The alkylation of *o*-cresol by camphene in the presence of 5 % ZrO$_2$/SO$_4^{2-}$ (450) at 80 °C, at the *o*-cresol/camphene molar ratio equal to 2 : 1 and the mass fraction of catalyst equal to 50 % resulted in obtaining *para*-alkylated 2-methylphenol with the isobornyl structure of the terpene substituent with the yield of 58 %.

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