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Acid Treated Montmorillonite—Eco-Friendly Clay as Catalyst in Carvone Isomerization to Carvacrol

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Abstract: Acid-treated montmorillonites (MMT) were used as catalysts of carvone isomerization to carvacrol. Mineral acids—sulfuric, hydrochloric, nitric acids and organic acids (acetic and chloroacetic)—were used for the acid treatment. Prepared materials were characterized by available characterization methods, namely XRD, EA, TPD, TPO, UV-Vis, laser light scattering and nitrogen physisorption. The structure of montmorillonite remained intact after treatment. However, TPD proved the increase of acidity of acid-treated materials comparing pure montmorillonite. All materials were tested in the isomerization of carvone, producing carvacrol as the desired product. The initial reaction rate increased using the materials in the row MMT-COOH < MMT-HNO3 < MMT-CICOOH < MMT-H2SO4 < MMT-HCl, which is in accordance with the pKa of acids used for the treatment. The number of weak acid sites strongly influenced the selectivity to carvacrol. The optimal solvent for the reaction was toluene. Total conversion of carvone and the selectivity to carvacrol 95.5% was achieved within 24 h under 80 ºC, with toluene as solvent and montmorillonite treated by chloroacetic acid as catalyst. The catalyst may be reused after calcination with only a low loss of activity.

Keywords: montmorillonite; isomerization; carvacrol; carvone

1. Introduction

Carvacrol (5-isopropyl-2-methylphenol) is a commonly used nontoxic fragrance and food additive. Carvacrol is contained in essential oil of oregano, thyme or savory. A large scale of carvacrol biologic effects (antibacterial, insecticidal, antifungal, analgetic, antioxidant or antiparasitic) was reported [1,2]. Moreover, carvacrol can be oxidized to obtain thymoquinone—a substance with possible anticancer, antioxidant and cholesterol lowering effects. Except natural resources, carvacrol can be synthesized by reaction of isopropylalcohol or 2-chlorpropane with o cresol catalyzed by iron(III) or aluminum(III) chloride [3,4] or more environmentally friendly isomerization of carvone, a naturally occurring substance. The last mentioned substance can be found, e.g., in caraway or spearmint essential oil [5,6]. Carvone occurs in the form of two optical isomers. (+)-carvone can be found as a main component of caraway (up to 60%) and dill essential oils, (−)-carvone is present in spearmint essential oil (70–80%) [7]. Carvone was formerly isolated by distillation of the above-mentioned essential oils; nowadays, synthesis from limonene is preferred [7].

Isomerization of carvone to carvacrol (Figure 1) can be catalyzed by organic or inorganic acid [8–10]—the use of p-toluene sulfonic acid and microwave irradiation led to 85% yield of carvacrol after 35 min (solvent 1,4-dioxane, 180 ºC) [10]. The use of 6 M sulfuric acid gave 95% yield (100 ºC, 30 min, without solvent) [9]. Solid ion exchange resins containing sulfoxyl groups are also reported in this isomerization, e.g., using Amberlyst 15 as catalyst 98% yield after 10 min was obtained (75 ºC) [9]. Palladium-based catalysts were also described in the carvone isomerization to carvacrol [11–14]. Pd-Al2O3 was used for isomerization in the gas phase: The influence of hydrogen and water content on reaction...
results was monitored (total selectivity of carvacrol formation was obtained at 150 °C using the ratio hydrogen:carvone 1:6 [13]). Palladium modified layered triple hydroxide (Ni-Mg-Al) was used in the studied isomerization, and 99% yield of carvacrol was obtained (150 °C, 30 min [14]). The usage of montmorillonite and clinoptilolite, which belong to the group of natural minerals, was reported. Yield of carvacrol > 96% was obtained (160 °C, toluene, 3 h [15]) in the case of montmorillonite. A natural zeolite—clinoptilolite was also catalytically active in carvone isomerization—yield of carvacrol > 90% was obtained in solvent-free synthesis (210 °C, 3 h [1]). Rare mentions of specific catalysts, e.g., complex of NHC ligand and palladium or Pt(IV) complex, can be also found [11,16].

![Reaction scheme of isomerization carvone to carvacrol.](image)

We focused our attention mostly on montmorillonite (alumosilicate with the structure Al₂Si₄O₁₀(OH)₂·nH₂O), the properties of which (acidity above all) can be tuned by treatment by mineral acid. The treatment would offer a cheap ecofriendly catalyst. Montmorillonite structure is formed from three layers, where octahedral layers of Al₂O₃ are located between layers of tetrahedral SiO₂ (e.g., [17,18]). Montmorillonite has a wide range of catalytic applications, which are connected with the presence of both Lewis and Brønsted acid sites. The positive effect on the acidity of montmorillonite caused by the acid treatment is widely discussed. Treatment with acid causes the exchange of some Na⁺ ions from montmorillonite with H⁺ from acid, which causes material acidity enhancement [19,20]. Acid treated montmorillonite was successfully used as catalyst in a wide range of reaction, e.g., α-terpineol synthesis from α-pinene [20], Prins reaction of benzaldehyde and isoprenol [19], Prins reaction of vanillin with isopulegol [21], methanol dehydration [22], benzene alkylation [22], production of fatty acid methyl esters [23,24] or Knovenagel condensation [25].

In this work, we would like to offer insight into possible use of acid-treated montmorillonite K10 as a catalyst for isomerization of carvone to carvacrol.

2. Materials and Methods
2.1. Modification of Montmorillonite K10

Montmorillonite K10 (10 g, Sigma Aldrich, St. Louis, MO, USA, 97%) was suspended in 50 mL of 1 M solution of acid in demineralized water (conductivity < 1 µS·cm⁻¹) and stirred overnight at room temperature. The material was then filtered (filter S4), washed with demineralized water until the filtrate was neutral and dried overnight (80 °C, air). Different acids were used for modification—sulfuric acid (96%, Penta, Praha, Czech Republic), hydrochloric acid (35%, Penta, Praha, Czech Republic), nitric acid (65%, Penta, Praha, Czech Republic), acetic acid (99%, Chemapol, Praha, Czech Republic) and chloroacetic acid (99%, Sigma Aldrich, St. Louis, MO, USA). Abbreviations of materials used in this article are summarized in Table 1.

2.2. Isomerization of Carvone to Carvacrol

In a typical experiment, catalyst (0.5 g, activated in oven at 80 °C overnight), solvent (3 mL) and carvone (6 mmol, 97%, Sigma Aldrich, St. Louis, MO, USA) under inert (argon) atmosphere were added to a round bottom flask under inert (argon) atmosphere. Reaction mixture was heated to 80 °C and stirred overnight (700 rpm). A large number of solvents were tested in this reaction—toluene, dimethyl sulfoxide, heptane, acetonitrile, N,N′-dimethylformamide, 1,4-dioxane, n-propylalcohol, acetonitrile (all p.a., Penta, Praha, Czech
Republic) and benzonitrile (99%, Aldrich, St. Luis, MO, USA). Samples were analyzed using gas chromatograph Shimadzu 17 A equipped with middle polar column ZB-50 and FID. Selectivity was calculated as an amount of originated carvacrol divided by carvone conversion. The average reaction rate was calculated according to our previous work [26]. The activation energy was calculated by linear regression using the Arrhenius equation.

| Abbreviation | Material |
|--------------|----------|
| MMT K10      | Nonmodified montmorillonite K10 |
| MMT-H$_2$SO$_4$ | Montmorillonite K10 treated with sulfuric acid |
| MMT-HNO$_3$  | Montmorillonite K10 treated with nitric acid |
| MMT-HCl      | Montmorillonite K10 treated with hydrochloric acid |
| MMT-COOH     | Montmorillonite K10 treated with acetic acid |
| MMT-CICOOH   | Montmorillonite K10 treated with chloroacetic acid |
| MMT-H$_2$SO$_4$-RE80 | Montmorillonite K10 treated with sulfuric acid recycled using temp. of 80 °C |
| MMT-H$_2$SO$_4$-RE300 | Montmorillonite K10 treated with sulfuric acid recycled using temp. of 300 °C |

2.3. Characterization of Materials

Temperature programmed desorption (TPD) of pyridine was performed to compare the acidity of all materials (AutoChem II Micromeritics Instrument 2920 was used, Unterschleissheim, Germany). A thermal conductivity detector (TCD) and quadrupole mass spectrometer (MKS Cirrus 2 Analyzer, MKS Instruments, Crewe, UK) with a capillary coupling system were used for the desorbed pyridine detection. A catalyst sample (0.1 g) was placed in a quartz U-shaped tube. Prior to adsorption of pyridine, the catalyst was heated under a helium flow (30 mL/min) up to 150 °C, and kept at 150 °C for 60 min to remove impurities from the sample, and clean the material surface. Measured pulses of pyridine (pulse volume, 5 mL) were injected into the helium gas and carried through the catalyst sample until adsorption saturation. Then, the sample was flushed with helium for 120 min to remove physisorbed pyridine. Afterward, the linear temperature program (10 °C/min) was started at a temperature of 150 °C and the sample was heated up to a temperature of 900 °C. The amount of desorbed pyridine was determined by calibration of the intensity of the 79 amu MS response (5 mL loop) [27–29].

Temperature programmed oxidation (TPO) was performed to analyze amount of carbonaceous deposits on reused catalysts. Autochem II 2920 (Micromeritics, Unterschleissheim, Germany). Both a thermal conductivity detector (TCD) and a quadrupole mass spectrometer (MKS Cirrus 2 Analyzer, MKS Instruments, Crewe, UK) with a capillary coupling system were used for originating carbon dioxide detection. Catalyst sample (0.09 g) was placed in a quartz U-shaped tube. Prior to TPO experiment, the catalyst was heated under a helium flow (30 mL/min) up to 80 °C, and kept at 80 °C for 20 min to dry catalyst. Afterwards, a catalyst was set up to O$_2$-He flow (10% O$_2$ in helium, 30 mL/min), and the linear temperature program (15 °C/min) started, and the sample was heated up to a temperature of 900 °C. The amount of originated carbon dioxide was determined by calibration of the intensity of the 44 amu MS response (0.5 mL loop).

The specific surface area was measured using nitrogen adsorption (3Flex volumetric analyzer, Micromeritics, Unterschleissheim, Germany), and calculated via the BET equation and $t$-plot method.

The particle size distributions of all samples were determined by laser light scattering (Malvern Mastersizer 3000 system equipped with Hydro EV wet sampling unit, Malvern Instruments Ltd., Malvern, UK). The materials were characterized using a wet dispersion method. The particle size distributions were recorded for at least five determinations for each sample at an obscuration range of 8–14%. The particle size distributions of all materials were determined using demineralized water (conductivity < 1 µS·cm$^{-1}$) with surfactant Triton X-100 (Aldrich) as a dispersion medium. The reference refractive index for all materials was 1.555.
Elemental analysis (EA) was performed to confirm that all acid used for modification was removed from material. The amount of carbon, hydrogen, nitrogen and sulfur was determined using Elementar vario EL Cube (Elementar, Langenselbod, Germany), and the amount of chlorine was detected using Multi EA5100 (Analytik Jena, Jena, Germany).

XRD powder data was measured at room temperature on θ-θ powder diffractometer X’Pert PRO (Malvern Instruments Ltd, Malvern, UK) in Bragg–Brentan parafocusing geometry with CoKα radiation (λ = 1.7903 Å, U = 35 kV, I = 40 mA).

XRF analysis was performed on WD-XRF ARL 9400 XP Spectrometer (Malvern Instruments Ltd., Malvern, UK).

Distinction of Lewis and Brønsted acid sites was performed by adsorption of pyridine using spectrophotometer (Shimadzu UV2600i, Shimadzu, Kyoto, Japan) with an integration sphere [30].

3. Results

3.1. Material Characterization

All prepared materials were characterized using various techniques. The methods were chosen to confirm the materials’ composition, and to find the properties that may influence their catalytic performance. The composition was determined by EA (Table 2).

| Material   | Nitrogen (%) | Carbon (%) | Hydrogen (%) | Sulfur (%) | Chlorine (ppm) |
|------------|--------------|------------|--------------|------------|----------------|
| MMT K10    | -            | -          | 1.07         | -          | -              |
| MMT-H₂SO₄  | -            | 0.27       | 1.03         | -          | -              |
| MMT-HNO₃   | -            | 0.18       | 1.12         | -          | 217            |
| MMT-HCl    | -            | 0.18       | 1.08         | -          | 225            |
| MMT-COOH   | -            | 0.14       | 1.21         | -          | 225            |

Raw montmorillonite K10 did not contain any carbon (as expected), which was the most considerable difference compared to all modified materials. In all acid-treated materials, a small amount of combustible carbon was present (0.14–0.27). No traces of sulfur and nitrogen were detected in any case, meaning acids (H₂SO₄, HNO₃) were successfully removed from the materials. A small amount (218 resp. 225 ppm) of chlorine was observed in the case of treating by acids containing chlorine. The overall small content of analyzed elements (C, Cl) and no content of S and N confirmed the successful washing out of acids used to treat montmorillonite K10. X-ray fluorescence (Table S1) results and X-ray diffraction (XRD) results were presented in our previous work [20,31]. XRD analysis revealed preserved montmorillonite structure after modification (Figure S1).

The treatment by acids was distinctively positive from the point of view of material acidity. Modifying montmorillonite with different acids led to an insignificant increase of this parameter, which is especially important in the catalytic properties (Table 3).

| Material   | ∑ Acid Sites | Weak Acid Sites | Strong Acid Sites |
|------------|--------------|-----------------|------------------|
| MMT K10    | 149          | 149             | -                |
| MMT-H₂SO₄  | 182          | 118             | 64               |
| MMT-HNO₃   | 153          | 117             | 36               |
| MMT-HCl    | 179          | 137             | 42               |
| MMT-COOH   | 184          | 129             | 55               |
| MMT-CICOOH | 172          | 132             | 40               |
Raw montmorillonite K10 contained only one temperature maximum (ca 270 °C) assigned to weak acid sites. Acid-treated montmorillonites also had this band at ca 270 °C. However, they also possessed a significant band with a maximum at 540 °C, which corresponded to strong acid sites (Figure S2). Origination of a new band correlates with the incorporation of new H\(^+\) ions into the material structure. Our observation follows previous statements that the surface composition of clay base materials is pH-dependent (e.g., [32]). The main groups responsible for montmorillonite acidity are \(\equiv M-OH\) and \(\equiv M-OH^2+\) (where M represents Si or Al). The treatment by sulfuric and nitric acids (MMT-H\(_2\)SO\(_4\), MMT-HNO\(_3\)) showed a significant decrease in amount of weak sites and the formation of strong sites. The treatment by chlorinated acids showed a low reduction of weak acid site amount and the formation of strong acid sites. Different behavior may be explained by the traces of chlorine in the materials, which might influence the overall acidity.

UV-Vis spectroscopy using adsorbed pyridine showed (Figure S3) the dominant presence of hydroxyl groups that are responsible for the catalytic properties. The most significant was the band at ca 39,900 cm\(^{-1}\) assignable to \(\pi-\pi^*\) excitation of pyridinium ion [30]. The bands of pure (without adsorbed pyridine) materials hid the bands potentially allocated to Lewis acid sites. However, we suppose that mainly Brønsted acid sites were present in all materials due to the preparation and drying methods. The differences between the materials were almost negligible.

Laser light scattering was used to monitor the particle size distribution of raw and acid-treated montmorillonite (Table 4, Figure 2). Curves of material volume density did not differ significantly. However, raw montmorillonite had a little higher Dv(50) value (17.4 µm) than acid-treated materials (11.3–13.7 µm), meaning that it contained slightly bigger particles. The stirring of the materials during the treatment was probably responsible for the change. Dv(10) values, i.e., the boundary value for 10% of the smallest particles, were very similar for all materials (3.07–3.69 µm). Raw and acid-treated materials, except for MMT-CH\(_3\)COOH, also contained a small amount of bigger particles with the size around 700 µm. Curves of raw [33,34] and acid-treated [20] materials are similar to already published results.

**Table 4.** Particle sizes measured using laser light scattering.

| Material       | Dv(10) (µm) | Dv(50) (µm) | Dv(90) (µm) |
|----------------|-------------|-------------|-------------|
| MMT K10        | 3.69        | 17.1        | 69.1        |
| MMT-H\(_2\)SO\(_4\) | 3.52        | 12.7        | 73.1        |
| MMT-HNO\(_3\)  | 3.45        | 13.7        | 74.6        |
| MMT-HCl        | 3.27        | 11.3        | 41.9        |
| MMT-COOH       | 3.10        | 11.7        | 46.9        |
| MMT-ClCOOH     | 3.07        | 11.5        | 46.6        |

**Figure 2.** Particle size distribution curves.
Nitrogen physisorption was used to compare material textural properties (Table 5, Figure 3). All samples of catalysts showed adsorption isotherms of type IVa (IUPAC classification). Samples consisted of only mesopores with classical type hysteresis loop H3 (IUPAC classification), which corresponded to non-rigid aggregates of plate-like particles (e.g., clays). Table 5 summarizes the results of the textural analyses of the catalysts. Total pore volume was 0.36 cm$^3$/g in all cases. Figure 3 compares the pore size distribution from N$_2$ adsorption for samples using the BJH method. Based on the results of the mesopores volume distribution (BJH method), all samples contained narrow mesopores (about 7 nm). Similar to the case of XRD, textural characteristics of raw and acid-treated montmorillonite were similar.

Table 5. Textural properties of materials obtained by nitrogen physisorption.

| Material       | S$_{BET}$ (m$^2$/g) | St-Plot (m$^2$/g) | t-Plot Micropore Volume (cm$^3$/g) |
|----------------|---------------------|-------------------|-----------------------------------|
| MMT K10        | 254                 | 246               | 0.0021                            |
| MMT-H$_2$SO$_4$| 263                 | 255               | 0.0021                            |
| MMT-HNO$_3$    | 271                 | 258               | 0.0038                            |
| MMT-HCl        | 268                 | 255               | 0.0046                            |
| MMT-COOH       | 263                 | 257               | 0.0013                            |
| MMT-CICOOH     | 271                 | 259               | 0.0043                            |

Temperature programmed oxidation (TPO) was used to determine the amount of carbonaceous residues on catalysts after reuse (Figure 4). Two types of recycling were performed—the first of them involved washing of catalyst with toluene and drying at 80 °C overnight (MMT-H$_2$SO$_4$-RE80); the second recycling process was similar—the only difference was calcination (300 °C) overnight (MMT-H$_2$SO$_4$-RE300). The assumption was that if any carbonaceous deposits were present on the material, carbon dioxide would originate during the TPO. The original amount of carbonaceous residues on material could be calculated from the amount of evolved carbon dioxide. In fresh MMT-H$_2$SO$_4$, a small amount of carbonaceous deposits was found on the material surface—2 mg$_{\text{carbon}}$/g$_{\text{mat}}$ (which was also confirmed using EA—2.7 mg$_{\text{carbon}}$/g$_{\text{mat}}$). Carbonaceous deposits were present in a higher amount in recycled materials—4 mg$_{\text{carbon}}$/g$_{\text{mat}}$ for MMT-H$_2$SO$_4$-RE300 and 8 mg$_{\text{carbon}}$/g$_{\text{mat}}$ for MMT-H$_2$SO$_4$-RE80. The organic compounds remaining in the structure were obviously the compounds from the reaction mixture. The recycling treatment should remove all of them from the material to enable the recovery of the catalyst activity.
Higher calcination temperature during catalyst recycling decreased carbonaceous residues compared to simple catalyst drying at 80 °C. All organic compounds should be removed from the material above 300 °C as carvone, carvacrol, and the used solvent have boiling points lower than this temperature. However, any used recycling process did not remove all carbonaceous compounds.

3.2. Catalytic Tests

Isomerization reactions are the reactions with relatively low activation energy. Thus, even low acidic catalysts may be used for these reactions. Our studied materials based on montmorillonite K10 also belong to this group. The simple treatment by acid increased the acidity of cheap and available montmorillonite. We tested its catalytic properties on the interesting isomerization of carvone to carvacrol (Figure 1).

Table 6 summarizes the influence of reaction conditions on the course of the studied reaction. Different treating of montmorillonite was one of the influencing factors together with solvent type, temperature and catalyst amount.

3.2.1. Influence of Acid Treatment Type

We studied the influence of acid used to modify raw montmorillonite on the reaction course at 80 °C (Table 6, rows 1–6). A significant positive effect of acid modification on the reaction course was observed. Raw montmorillonite provided only 26% conversion of carvone after 24 h of reaction. The conversion > 99% was obtained using MMT-H$_2$SO$_4$, MMT-HCl, MMT-HNO$_3$ and MMT-CICOOH (24 h). Using MMT-CH$_3$COOH, 76% conversion of carvacrol was obtained (24 h). The reaction rate using treated MMTs increased in the row MMT-COOH < MMT-HNO$_3$ < MMT-CICOOH < MMT-H$_2$SO$_4$ < MMT-HCl. The increase was almost in all cases in accordance with the pKa of acids [35] used for the treatment (Figure 5). The only exception was chloroacetic acid, whose behavior might be connected with chlorine remaining in the structure. Chlorine might be responsible for the higher activity of the materials, as we discussed in the EA section. Chlorine influence is also visible at a significantly higher rate in the case of hydrochloric acid.
Table 6. Reaction result using different reaction conditions (solvent 3 mL, carvone 6 mmol, 24 h), selectivity to carvacrol.

| Row | Cat.            | Temp. (°C) | Cat. Amount (g) | Solvent | Conversion (24 h, %) | Selectivity (24 h, %) | Selectivity (at 50% Conv., %) | Average Reaction Rate (mmol g$^{-1}$ min$^{-1}$) |
|-----|-----------------|------------|-----------------|---------|----------------------|------------------------|-------------------------------|----------------------------------|
| 1   | MMT K10         |            |                 |         | 26.1                 | 24.5                   | -                             | 0.24                             |
| 2   | MMT-HNO$_3$     |            |                 |         | 99.9                 | 79.9                   | 55.4                          | 2.88                             |
| 3   | MMT-HCl         |            |                 |         | 99.9                 | 84.5                   | 87.2                          | 9.76                             |
| 4   | MMT-COOH        | 80         | 0.5             | toluene | 75.9                 | 73.6                   | 81.4                          | 1.12                             |
| 5   | MMT-CICOOH      |            |                 |         | 99.9                 | 95.5                   | 82.1                          | 3.92                             |
| 6   | MMT-HCl         | 80         | 0.5             | heptane | 99.5                 | 83.1                   | 77.8                          | 4.92                             |
| 7   | MMT-COOH        |            |                 |         | 11.3                 | 45.1                   | -                             | -                                |
| 8   | MMT-HNO$_3$     |            |                 |         | 82.2                 | 68.6                   | 57.8                          | 0.76                             |
| 9   | MMT-ClCOOH      |            |                 |         | 56.6                 | 6.5                    | 2.2                           | 0.0007                           |
| 10  | MMT-H$_2$SO$_4$ | 70         |                 |         | 93.8 *               | 98.6 *                 | 78.6                          | 5.81                             |
| 11  | MMT-H$_2$SO$_4$ | 90         |                 |         | 26.6                 | 38.0                   | -                             | 0.40                             |
| 12  | MMT-H$_2$SO$_4$ | 90         |                 |         | 100                  | 94.1                   | 85.4                          | 6.44                             |
| 13  | MMT-H$_2$SO$_4$ |            |                 | none    | 6.8                  | 50.1                   | -                             | 0.02                             |
| 14  | MMT-H$_2$SO$_4$ | 80         | 0.075           | toluene | 34.1                 | 45.9                   | -                             | 0.36                             |
| 15  | MMT-H$_2$SO$_4$ |            |                 |         | 67.2                 | 99.9                   | 97.2                          | 1.01                             |
| 16  | MMT-H$_2$SO$_4$ |            |                 |         | 87.3                 | 99.9                   | 99.9                          | 2.02                             |

* after 6 h of reaction.

Figure 5. Dependence of reaction rate on pKa of the acid used for treatment.

We have not found the connection between either total acidity or strong acidity of materials and the reaction rate (Figure S4).

Two undesired products occurred in the reaction mixture. 8-hydroxycarvone and dicarvone (Figure 6), beside the desired product.

Figure 6. Undesired products identified in reaction mixture: 8-hydroxycarvone (a) and dicarvone (b).
Raw montmorillonite also provided the lowest selectivity of carvacrol formation (24.5%). The highest selectivity to carvacrol at 50% conversion of carvone (87%) was obtained using material MMT-HCl. Origination of 8-hydroxycarvone is probably connected with (i) a trace amount of water in the used toluene or (ii) the water molecules on the surface of the used catalysts (Figure S6). The amount of 8-hydroxycarvone in the reaction mixture, especially in some experiments, confirmed the latter mentioned option. The selectivity (in contrast to reaction rate) was dependent on the type of acid site present on the surface (Figure 7). Total acidity seemed not to influence the selectivity. In contrast, the amount of weak acid sites influences the selectivity at 50% conversion positively. With increasing conversion, the achieved selectivity increased. The influence of strong acid sites is not so clear because these centers might catalyze preferably side reactions, especially the carvone hydration.

![Dependence of selectivity at 50% conversion on the strength of acid sites.](image)

The selectivity after 24 h was similar for almost all reactions, except MMT-COOH, which was only 74%, and MMT-CICOOH, which was 96%. We can divide the materials based on the selectivity increase or decrease with increasing conversion. In the first group, to which belong MCMT-COOH and MMT-HCl, the selectivity decreased with the increasing conversion, which is a typical phenomenon. To the second group belong MMT-HNO₃, MMT-CICOOH and MMT-H₂SO₄. In the second group are the materials we used to observe 8-hydroxycarvone as the main by-product. From 8-hydroxycarvone by dehydration and isomerization process, the desired carvacrol might be formed (Figure S5). The by-product was an intermediate of the reaction that explained the increase of the selectivity with increasing conversion.

### 3.2.2. Influence of the Solvent

Solvent influence on the course of any reaction can be crucial [36]. The solvent influence on our reaction is visible in Table 6, rows 6–10. The most suitable solvent from all tested was toluene. The selectivity was 83% at 99% conversion in toluene. Similar results were obtained using heptane; however, the reaction rate in this solvent was significantly lower. A low reaction rate might be caused by the different properties of both nonpolar solvents, e.g., the solubility of reactants. We also tested two polar solvents—benzonitrile and n-propanol. Polar solvents, in some cases, might boost the activity of clay catalysts due to their swelling properties. We suppose the partial swelling effect in n-propanol because not so low conversion was achieved in this solvent. Still, the selectivity to desired carvacrol was very low. The undesired product formed in such reaction mixture was ketal of n-propanol...
and carvone. Low selectivity was also detected in the reaction mixture using benzonitrile. However, in that case, the main undesired products were 8-hydroxycarvone and dicarvone. We suppose that polar solvents interacted with the active sites of used catalysts.

We also tested the reaction without any solvent (Table 6, row 10). The reaction rate the same as the selectivity to desired carvacrol was the highest when no solvent was used. This result confirmed our theory that the polar solvent would interact with the active sites of the catalyst. When no solvent was present or nonpolar solvents were used, the most polar substance was carvone, which should interact with the active sites, forming the desired product. However, more polar carvacrol would also block the active sites and remain on the catalyst surface. The product might be the most probable cause of catalyst deactivation together with compounds with a higher boiling point.

3.2.3. The Influence of the Temperature and Catalyst Amount

The influence of the temperature on the course of the studied reaction was as expected (Table 6, rows 6, 11, 12). With the increasing temperature, the reaction rate increased. Very low reaction rate at 70 °C showed that the catalyst was almost inactive under this temperature, and it was evident that at least 80 °C should be used. The apparent activation energy was calculated (15–28 kJ/mol) based on the Arrhenius equation. Still, its value was strongly influenced by the low activity of the used catalyst under a temperature lower than 80 °C. The main byproduct responsible for the low selectivity was 8-hydroxycarvone. This compound (as we have described above) might serve as an intermediate in the formation of desired carvacrol. The transformation of the intermediate to the desired product also proceeded with the low reaction rate.

The catalyst amount significantly influenced the reaction rate as expected. Surprisingly, the increase of the catalyst amount less than twice increased the rate (0.3 g to 0.5 g) more than 10 times (Table 6, rows 6, 13, 14). The increase might be connected with the blockage of acid sites by the product, as we have discussed above, in part dealing with the solvent influence. However, either the washing of the catalyst surface or calcination of the used material might solve the blockage of the catalyst’s active sites. By those procedures, the material might be reused, and it would eliminate the disadvantages of the necessity of high catalyst amount. The low rate of the production of carvacrol from the reaction of intermediates was also responsible for the low selectivity.

3.2.4. The Catalyst Reuse

The catalyst recovery by two approaches partially confirmed our supposition about the blockage of the active sites by the product (Table 6, rows 6, 15, 16). When the catalyst was filtered from the reaction mixture, washed by the solvent and dried at 80 °C, the reaction rate was significantly lower than using a fresh catalyst. More efficient was the replacement of drying by calcination at a higher temperature (300 °C). The reaction rate in such cases did not achieve such a high value, as in the case of the fresh catalyst; however, it was twice as high as in the case of only a dried catalyst. This means that used processes partly removed the carbonaceous compounds attached to the catalyst surface. A higher temperature (e.g., 550 °C) would be convenient for total regeneration. However, collapse of the montmorillonite structure under such temperature might occur. Repeated use of the catalyst had a positive effect on the selectivity to carvacrol. In both cases, almost 100% selectivity was achieved. We suppose that the active centers of the catalyst responsible for the reaction leading especially to 8-hydroxycarvone (centers responsible for hydration of carvone) either remained occupied by carbonaceous compounds or changed during the reaction process. Nevertheless, we can say that montmorillonite-based catalysts may be reused in our studied reaction with low loss of activity and no loss of selectivity.

3.2.5. Proposed Mechanism of Carvone Isomerization to Carvacrol

From our findings, the mechanism of carvone isomerization carvacrol consists of the four subsequent steps—(i) protonation of C-C double bond in the side chain of carvone to
form carbocation, (ii) carbocation rearrangement, (iii) formation of new C-C double bond in cyclohexane skeleton of carvone and (iv) enolization (Figure 8).

![Figure 8. Proposed reaction mechanism for carvacrol formation from carvone.](image)

**4. Conclusions**

We used five acids for the treatment of montmorillonite K10 (MMT)—mineral acids (sulfuric, hydrochloric and nitric) and organic acids (acetic and chloroacetic). The acid-treated materials were characterized by XRD, EA, UV-Vis, TPD, TPO, laser light scattering and nitrogen physisorption. The methods showed an increase in the amount of acid sites after the acid treatment and preservation of the montmorillonite structure. EA confirmed the total release of acids after the treatment, which showed that the acid sites of the material surface are responsible for the catalytic properties. The catalytic properties were tested in the model reaction of carvone isomerization to carvacrol. The catalytic activity (expressed as the reaction rate) decreased in the row MMT-HCl > MMT-H2SO4 > MMT-CICOOH > MMT-HNO3 > MMT-COOH. The reaction rate decreased with the increasing value of pKa of the acids used for the treatment. According to the literary data, the formation of acid sites is pH-dependent. Thus our finding confirmed this information. The selectivity to carvacrol was dependent on the amount of weak acid sites present on the catalyst surface. When the amount of weak acid sites increased, the selectivity to carvacrol increased. However, the main by-product decreasing the selectivity was 8-hydroxycarvone, which may serve as an intermediate for producing the desired carvacrol. The polar solvents may interact with the catalyst surface and block the active sites necessary for the isomerization reaction. Thus, we recommend the used of nonpolar solvents. The reuse of the catalyst showed only a low decrease in the reaction rate and no loss of selectivity. It was necessary to perform the calcination at at least 300 °C between the reaction cycles. The used calcination temperature might be the reason for the activity decrease because part of the acid sites might be removed. We have proven the possible use of montmorillonite-based catalysts and the positive effect of the acid treatment on its performance in the potentially important isomerization of carvone to carvacrol. The other advantages are the use of cheap acids for the treatment, the simplicity of the modification process and the possibility of catalyst reuse. We also want to mention that achieved selectivity 95.5% to desired carvacrol at total conversion of carvone is almost the best result achieved in this process up to now.
Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/reactions2040031/s1, Figure S1: XRD results for raw and acid-treated montmorillonite, Figure S2: TPD-MS results for raw and acid-treated montmorillonite (m/z = 79 signal), Figure S3: UV-Vis results for raw and acid-treated montmorillonite, Figure S4: Dependence of reaction rate on material acidity, Figure S5: Offered mechanism for carvacrol formation from 8-hydroxyxcarvone, Figure S6: Offered mechanism for 8-hydroxycarvone formation from carvone, Table S1: XRF analysis results.

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References
1. Wróbłewska, A.; Retajczyk, M. The Isomerization of S-Carvone over the Natural Clinoptilolite as the Catalyst: The Influence of Reaction Time, Temperature and Catalyst Content. React. Kinet. Mech. Catal. 2020, 130, 273–288. [CrossRef]
2. Alokam, R.; Jeankumar, V.U.; Sridevi, J.P.; Matikonda, S.S.; Peddi, S.; Alvala, M.; Yogeesswari, P.; Sriram, D. Identification and Structure–Activity Relationship Study of Carvacrol Derivatives as Mycobacterium Tuberculosis Chorismate Mutase Inhibitors. J. Enzyme Inhib. Med. Chem. 2014, 29, 547–554. [CrossRef] [PubMed]
3. Yadav, G.D.; Kamble, S.B. Synthesis of Carvacrol by Friedel–Crafts Alkylation of o-Cresol with Isopropanol Using Superacidic Catalyst UDCat-S. J. Chem. Technol. Biotechnol. 2009, 84, 1499–1508. [CrossRef]
4. Marinelli, L.; Di Stefano, A.; Cacciatore, I. Carvacrol and its derivatives as antibacterial agents. Phytochem. Rev. 2018, 17, 903–921. [CrossRef]
5. Kjonaas, R.A.; Mattingly, S.P. Acid-Catalyzed Isomerization of Carvone to Carvacrol. J. Chem. Educ. 2005, 82, 1813. [CrossRef]
6. De Carvalho, C.C.C.R.; da Fonseca, M.M.R. Carvone: Why and How Should One Bother to Produce This Terpene. Food Chem. 2006, 95, 413–422. [CrossRef]
7. Fahlbusch, K.-G.; Hammerschmidt, F.-J.; Panten, J.; Pickenhagen, W.; Schatkowski, D.; Bauer, K.; Garbe, D.; Surburg, H. Ullmann’s Encyclopedia of Industrial Chemistry II Flavors and Fragrances; Wiley-VCH-Verl.: Weinheim, Germany, 2020; p. 105.
8. Ritter, J.J.; Ginsburg, D. The Action of F-Butyl Hypochlorite on a-Pinene 1,2. J. Am. Chem. Soc. 1950, 72, 2381–2384. [CrossRef]
9. Gozzi, C.; Convard, A.; Husset, M. Heterogeneous Acid-Catalysed Isomerization of Carvone to Carvacrol. React. Kinet. Catal. Lett. 2009, 97, 301–306. [CrossRef]
10. Raner, K.D.; Strauss, C.R.; Trainor, R.W.; Thor, J.S. A New Microwave Reactor for Batchwise Organic Synthesis. J. Org. Chem. 1995, 60, 2456–2460. [CrossRef]
11. Heckenroth, M.; Khlebnikov, V.; Neels, A.; Schurtenberger, P.; Albrecht, M. Catalytic Hydrogenation Using Abnormal N-Heterocyclic Carbene Palladium Complexes: Catalytic Scope and Mechanistic Insights. ChemCatChem 2011, 3, 167–173. [CrossRef]
12. Benavente, P.; Cárdenas-Lizana, F.; Keane, M.A. Promotional Effect of Water in the Clean Continuous Production of Carvacrol from Carvone. Catal. Today 2018, 308, 45–49. [CrossRef]
13. Benavente, P.; Cárdenas-Lizana, F.; Keane, M.A. Selective Production of Carvacrol from Carvone over Supported Pd Catalysts. Catal. Commun. 2017, 96, 37–40. [CrossRef]
14. Jin, X.; Taniguchi, K.; Yamaguchi, K.; Nozaki, K.; Mizuno, N. A Ni–Mg–Al Layered Triple Hydroxide-Supported Pd Catalyst for Heterogeneous Acceptorless Dehydrogenative Aromatization. Chem. Commun. 2017, 53, 5267–5270. [CrossRef]
15. Liu, X.; Li, S.; Wu, Q.; Wan, M.; Zhang, J.; Liu, Y.; Tang, H. CN105523897A: A Synthetic Method of Carvacrol; Huai'an Wanbang Aromatic Chemicals Industry Co., Ltd.: Huaiian, China, 2015. Available online: https://patents.google.com/patent/CN105523897A/en (accessed on 10 November 2021).
16. Zheng, S.; Zhang, J.; Shen, Z. Platinum(IV)-Catalyzed Synthesis of Unsymmetrical Polysubstituted Benzenes via Intramolecular Cycloaromatization Reaction. Adv. Synth. Catal. 2015, 357, 2803–2808. [CrossRef]
17. Kim, H.-M.; Ob, J.-M. Physico-chemical interaction between clay minerals and albumin protein according to the type of clay. Minerals 2019, 9, 396. [CrossRef]
18. Norhayati, M.N.; Uan Noor Maznee, T.J.; Hoong, S.S.; Nurul’Ain, H.; Srihanum, A.; Kosheela Devi, P.P.; Mohd Norhisham, S.; Yeong, S.K.; Hazimah, A.H. Reproducibility of palm-based polysols production. J. Oil Palm Res. 2016, 28, 114–120.
19. Vyškočilová, E.; Gruberová, A.; Shamzhy, M.; Vrbková, E.; Krupka, J.; Červený, L. Prins cyclization in 4-methyl-2-phenyltetrahydro-2Hpyran-4-ol preparation using smectite clay as catalyst. React. Kinet. Mech. Cat. 2018, 124, 711–725. [CrossRef]
20. Sekerová, L.; Černá, H.; Vyskočilová, E.; Vrbková, E.; Červený, L. Preparation of α-Terpineol from Biomass Resource Catalysed by Acid Treated Montmorillonite K10. Catal. Lett. 2021, ahead of print. [CrossRef]

21. Timofeeva, M.N.; Volcho, K.P.; Mikhalchenko, O.S.; Panchenko, V.N.; Krupskaya, V.V.; Tsybulya, S.V.; Gil, A.; Vicente, M.A.; Salakhutdinov, N.F. Synthesis of octahydro-2H-chromen-4-ol from vanillin and isopulegol over acid modified montmorillonite clays: Effect of acidity on the Prins cyclization. J. Mol. Catal. A Chem. 2015, 398, 26–34. [CrossRef]

22. Ravichandran, J.; Sivasankar, B. Properties and Catalytic Activity of Acid-Modified Montmorillonite and Vermiculite. Clays Clay Miner. 1997, 45, 854–858. [CrossRef]

23. Zatta, L.; Paiva, E.J.M.; Corazza, M.L.; Wypych, F.; Ramos, L.P. The Use of Acid-Activated Montmorillonite as a Solid Catalyst for the Production of Fatty Acid Methyl Esters. Energy Fuels 2014, 28, 5834–5840. [CrossRef]

24. Luna, F.M.T.; Cecilia, J.A.; Saboya, R.M.A.; Barrera, D.; Sapag, K.; Rodríguez-Castellón, E.; Cavalcante, C.L. Natural and Modified Montmorillonite Clays as Catalysts for Synthesis of Biolubricants. Materials 2018, 11, 1764. [CrossRef]

25. Varadwaj, G.B.B.; Rana, S.; Parida, K.M. Amine functionalized K10 montmorillonite: A solid acid–base catalyst for the Knoevenagel condensation reaction. Dalton Trans. 2013, 42, 5122–5129. [CrossRef] [PubMed]

26. Vrbková, E.; Šteflová, B.; Sekerová, L.; Krupka, J.; Vyskočilová, E.; Červený, L. Heterogeneous Mo/W/Zn–SiO2 based catalysts in nopol (2-(6,6-dimethyl-2-bicyclo[3.1.1]hept-2-enyl)ethanol) synthesis. React. Kinet. Mech. Cat. 2020, 131, 213–232. [CrossRef]

27. Vrbková, E.; Šteflová, B.; Sekerová, L.; Krupka, J.; Vyskočilová, E.; Červený, L. Contribution to MoO3–SiO2 and WO3–SiO2 utilization—active catalysts in jasmine aldehyde, 2-hexyl-1,3-dioxolane and methylaurate synthesis. React. Kinet. Mech. Cat. 2020, 129, 645–658. [CrossRef]

28. Vrbková, E.; Šteflová, B.; Zapletal, M.; Vyskočilová, E.; Červený, L. Tungsten oxide-based materials as effective catalysts in isopulegol formation by intramolecular Prins reaction of citronellal. Res. Chem. Intermed. 2020, 46, 4047–4059. [CrossRef]

29. Vrbková, E.; Prejza, T.; Lhotka, M.; Vyskočilová, E.; Červený, L. Fe-Modified Zeolite BETA as an Active Catalyst for Intramolecular Prins Cyclization of Citronellal. Catal. Lett. 2021, 151, 1993–2003. [CrossRef]

30. Velthoen, M.E.Z.; Nab, S.; Weckhuysen, B.M. Probing acid sites in solid catalysts with pyridine UV-Vis spectroscopy. Phys. Chem. Chem. Phys. 2018, 20, 21647–21659. [CrossRef]

31. Sekerová, L.; Spáčilová, M.; Vyskočilová, E.; Krupka, J.; Červený, L. Acid catalyzed acetalization of aldehydes with diols resulting into the formation of fragrant cyclic acetals. React. Kinet. Mech. Cat. 2019, 127, 727–740. [CrossRef]

32. Liu, Y.; Alessi, D.S.; Flynn, S.L.; Alam, M.S.; Hao, W.; Gingras, M.; Zhao, H.; Konhauser, K.O. Acid-base properties of 23. kaolinite, montmorillonite and illite at marine ionic strength. Chem. Geol. 2018, 483, 191–200. [CrossRef]

33. Vyskočilová, E.; Vrbková, E.; Trejbál, J.; Vaňková, M.; Červený, L. Eco-Friendly Natural Clay: Montmorillonite Modified with Nickel or Ruthenium as an Effective Catalyst in Gamma-Valerolactone Synthesis. Catal. Lett. 2021, ahead of print. [CrossRef]

34. Ma, X.; Fan, Y.; Dong, X.; Chen, R.; Li, H.; Sun, D.; Yao, S. Impact of Clay Minerals on the Dewatering of Coal Slurry: An Experimental and Molecular-Simulation Study. Minerals 2018, 8, 400. [CrossRef]

35. Chimni, S.S.; Singh, S.; Kumar, A. The pH of the reaction controls the stereoselectivity of organocatalyzed direct aldol reactions in water. Tetrahedron Asymmetry 2009, 20, 1722–1724. [CrossRef]

36. Vrbková, E.; Vyskočilová, E.; Lhotka, M.; Červený, L. Solvent Influence on Selectivity in α-Pinene Oxide Isomerization Using MoO3-Modified Zeolite BETA. Catalysts 2020, 10, 1244. [CrossRef]