

Aldol condensation of campholenic aldehyde and MEK over activated hydrotalcites

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Available online 21 June 2006

Abstract

In this paper, activated Mg–Al hydrotalcites were used as catalysts in the aldol condensation of campholenic aldehyde and methyl ethyl ketone (MEK). These materials represent an attractive alternative to less environmentally friendly liquid bases in a number of base-catalyzed reactions involved in the pharmaceutical and fragrance industries. The presence of basic hydroxyl groups in the interlayer space leads to very active materials. However, the relation between the activity of reconstructed hydrotalcites and the rehydration procedure is still not well understood. Different rehydration protocols in combination with extensive characterization studies were performed, including XRD, SEM, IR spectroscopy and TPD of CH₃CN and CH₃NO₂. The materials were tested as catalysts in the aldol condensation of campholenic aldehyde and MEK, and relationships between the catalytic performance of the activated hydrotalcites and the rehydration procedure were derived. Several factors may influence the activity and selectivity of this reaction, such as the reaction temperature, the molar ratio of the reactants and the degree of rehydration of the hydrotalcite-like catalysts. The selectivity towards the formation of the desired branched isomer increases when performing the reaction at low temperatures.

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Keywords: Solid base catalysis; Aldol condensation; Campholenic aldehyde; MEK; Hydrotalcite; Meixnerite; Rehydration

1. Introduction

Among a number of terpenes, α -pinene (**1**) is an important compound for the synthesis of a variety of aroma chemicals. Besides, its epoxide (**2**) can be isomerized to produce campholenic aldehyde (**3**) (Fig. 1a) [1]. The latter is a main intermediate in the synthesis of sandalwood fragrances, which are large-scale products in the flavor and perfume industry. The aldol condensation between (**3**) and methyl ethyl ketone (MEK) (**4**) (Fig. 1b) produces organic precursors (3-methyl-5-(2,2,3-trimethylcyclopent-3-enyl) pent-3-en-2-one (**5**) and 6-(2,2,3-trimethylcyclopent-3-enyl) hex-4-en-3-one (**6**)), applied in the synthesis of commercial sandalwood-type odorants such as Polysantol[®] and related compounds. Industrially, this reaction is performed using liquid bases such as NaOH or KOH as

homogeneous catalysts [2,3]. However, this practice presents important drawbacks, such as corrosion, waste generation and costly catalyst separation and re-use. Some undesired reactions such as the self-condensation of campholenal and secondary reactions involving the products produced can also be observed, making purification necessary by a costly washing operation, followed by neutralization and distillation steps to remove by-products. In this sense, the environmental factor reported by Sheldon, as a measure of the amount (kg) of by-products produced per kg of product in the fine chemical industry, displays a value in the range of 5–50 [4,5]. Consequently, the substitution of these bases by efficient solid catalysts will clearly lead to more sustainable and ecoefficient routes for the production of fine chemicals. Calcined Mg–Al layered double hydroxides (LDH) have been used for the aldol reaction between (**3**) and (**4**), and they gave a conversion of 100% after 1 h at 357 K with a selectivity around 97% for the overall mixture of the products (**5**) and (**6**) [6]. The production of (**5**) is desired over (**6**) because the alcohol derived from deconjugation and reduction has a stronger

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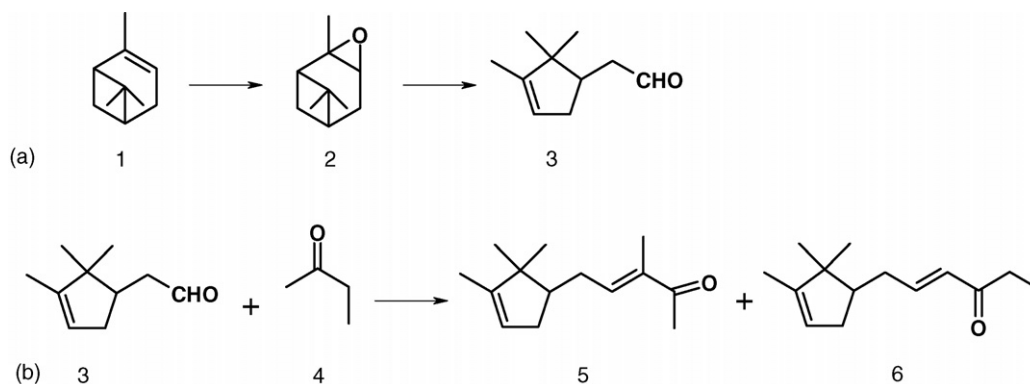


Fig. 1. (a) Epoxidation and isomerization of α -pinene epoxide (2) to campholenic aldehyde (3) and (b) aldol condensation of campholenic aldehyde (3) and MEK (4) to 3-methyl-5-(2,2,3-trimethylcyclopent-3-enyl) pent-3-en-2-one (5) and 6-(2,2,3-trimethylcyclopent-3-enyl) hex-4-en-3-one (6).

odor than the alcohol derived from (6). However, the presence of (6) does not affect the final properties of the product [3]. To the best of our knowledge, the reaction parameters impacting the selectivity between (5) and (6), and their relation with the nature of the catalyst applied have not been identified so far.

In recent years, LDHs (layered double hydroxides, also known as hydrotalcite-like compounds) have seen a growing interest for their use as solid catalysts, particularly in liquid-phase aldol condensations, e.g. benzaldehyde and acetone [7], citral and acetone [8–10], and the self-condensation of acetone [11]. These materials are described by the general formula $[M_n^{2+}M_m^{3+}(\text{OH})_{2(n+m)}]^{m+}[A^{x-}]_{m/x} \cdot y\text{H}_2\text{O}$, where M^{2+} and M^{3+} are di- and trivalent metal cations, respectively, A represents the x -valent anion (typically carbonate), which is needed to compensate the net positive charge of the brucite-like layers, and y is the number of water molecules in the interlayer space [12]. Due to the features of the Mg–Al LDH, thermal activation leads to mixed oxides Mg(Al)O, presenting acid–base pair sites with strong basic character. However, after rehydration of Mg(Al)O, due to its well-known memory effect, the reconstruction of the layered structure leads to catalysts with OH^- as compensating anions, exhibiting Brønsted basic properties. Recent studies established that the catalytic properties are strongly influenced by the accessibility of the active sites, which can be improved by the rehydration procedure [13]. Indeed, the dramatic increase of the specific surface area observed with samples rehydrated in the liquid phase rather than in the vapor phase (18 times higher), resulted in a higher activity in the condensation of citral and acetone [13]. Moreover, the samples rehydrated in the liquid phase, using ultrasound or a high stirring speed, formed very small and thin nanoplatelets as compared to those rehydrated in the vapor phase [14]. Therefore, a correlation between the amount of exposed OH^- sites (at the edges of the nanoplatelets) and the catalytic activity was obtained.

In this work we have investigated the performance of Mg/Al hydrotalcites and the materials derived from calcination and rehydration in the aldol condensation reaction between (3) and (4). Brønsted-type basic sites are generally recognized to be more active than Lewis-type basic sites in aldol condensation reactions, but their influence on the selectivity in the target

reaction has not been examined. The structure, morphology and basicity of the materials were extensively characterized by X-ray diffraction, SEM, FT-IR spectroscopy and TPD of two different probe molecules (CH_3CN and CH_3NO_2). Relationships between the activity and the selectivity for products (5) and (6) associated with the properties of the materials and reaction conditions have been derived.

2. Experimental

2.1. Materials

Mg–Al hydrotalcite (molar Mg/Al ratio = 3) was prepared by a co-precipitation method at constant pH (10 ± 0.2) of an aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.75 M) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.25 M) and a second solution of NaOH/ Na_2CO_3 (1 M of each). Both solutions were mixed dropwise under stirring at 298 K. After addition of the reactants, the slurry was aged at 298 K for 15 h under vigorous stirring. The obtained precipitate was filtered and thoroughly washed with large amounts of deionized water in order to remove Na^+ and NO_3^- ions. The solid was dried at 373 K for 18 h, yielding the as-synthesized hydrotalcite (HT_{AS}).

The HT_{AS} sample was thermally decomposed in air at a rate of 5 K min^{-1} to 723 K and was maintained at this temperature for 15 h in order to obtain the corresponding Mg–Al mixed oxide (HT_{C}). This material was rehydrated in decarbonated water by flowing argon (1 g of sample in 100 ml of water previously boiled under argon) for 1 h at room temperature and under mechanical stirring (700 rpm) or, alternatively, using ultrasounds for 5 min. After the rehydration process, the samples were filtered, washed with ethanol and dried under argon, yielding $\text{HT}_{\text{RL-MS}}$ or $\text{HT}_{\text{RL-US}}$, respectively.

2.2. Characterization

The chemical composition of the samples was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) in a Perkin-Elmer Plasma 400. The samples were diluted in 10 vol.% HNO_3 solution before analysis. C–N–H analysis was performed in a Carlo Erba EA1108 instrument.

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