

Effect of acetone/citral molar ratio and reaction conditions in the aldol condensation of citral with acetone catalyzed by a Mg,Al-mixed oxide

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Abstract

The aldol condensation of citral with acetone catalyzed by a Mg,Al-mixed oxide derived from hydrotalcite with an Al/(Al + Mg) molar ratio equal to 0.2 was studied. The influence of reaction parameters such as acetone/citral molar ratio (1–5), temperature (343–398 K), and reaction time (30–240 min) was evaluated aiming at their optimization to increase pseudoionone production with high selectivity. The best results were obtained for an acetone/citral molar ratio of 5 with 5 wt.% of catalyst (based in the total weight of reactants). The highest pseudoionone selectivity (90%) was achieved at 343 K after 4 h of reaction, with a citral conversion close to 50%. The observed trends suggest that higher conversions and selectivities should be attained at longer reaction times at 343 K. GC–MS analyses confirmed pseudoionone isomers as the main reaction products, the by-products being those from the aldol condensation between pseudoionone and acetone and from the self-condensation of citral. A general reaction scheme is proposed.

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1. Introduction

α - and β -Ionone (4'-(2,6,6-trimethyl-1-cyclohexenyl)-3-buten-2'-one) are products derived from essential oils with extensive use in soap and fragrances industries. β -Ionone is also important as precursor in the synthesis of vitamin A and other carotenoids. Ionones are commercially produced from homogeneous catalytic processes involving several unit operations. The first step (Fig. 1) is the production of pseudoionone (6,10-dimethyl-3,5,9-undeca-trien-2-one) from the aldol condensation of citral (3,7-dimethyl-2,6-octadienal) with acetone (propanone) catalyzed by alkaline hydroxides such as aqueous barium hydroxide, alcoholic sodium ethoxide, metallic sodium (which is pre-dissolved in alcohol), and alcoholic sodium hydroxide [1]. Some patents claim the use

of aqueous sodium hydroxide [2,3], sodium alcoxide [3] or lithium hydroxide [4] as catalysts. Pseudoionone (PSI) selectivities close to 80% are reported for citral conversions near 60%. The second step is the cyclization of pseudoionones forming the ionones. Depending on the strength of the acid used as catalyst, α - or β -ionone is produced. The alpha isomer is obtained in the presence of weak acids, such as phosphoric acid, and when a strong acid is the catalyst, such as sulfuric acid, β -ionone is formed [5].

With these homogeneous catalysts some undesired reactions such as the self-condensation of citral and secondary reactions involving the pseudoionones produced are also observed, making it necessary the purification of the latter by a laborious and costly washing operation followed by a careful fractional distillation to remove by-products with close boiling points. The distillation step exposes the product to prolonged heating in the presence of traces of either the alkaline catalyst or any acid used to remove it, thus favoring its decomposition with the formation of more by-products.

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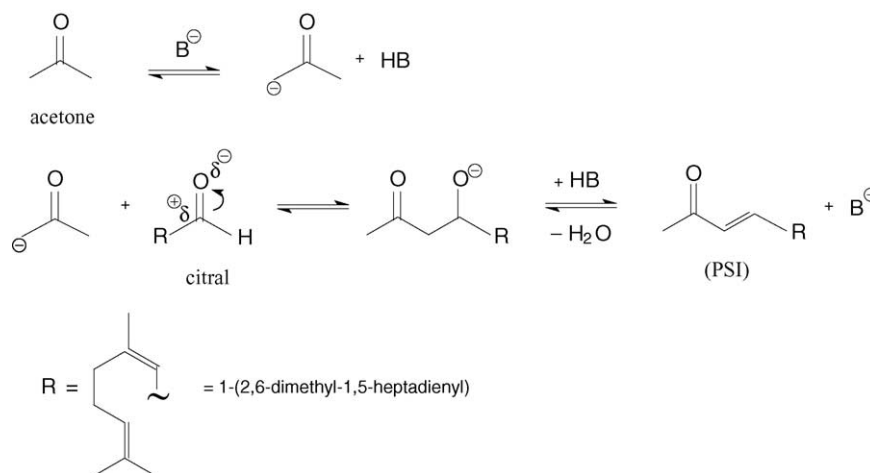


Fig. 1. Mechanism of aldol condensation between citral and acetone.

Moreover, for satisfactory yields, these processes demand the use of a large excess of acetone, typically 10–20 moles per mole of citral, thus requiring a large and costly plant for commercial production [4].

The substitution of this conventional homogeneous process by a heterogeneous one is a matter of great interest due to the possibility of reducing the consumption of reactants and the number of operations involved. For example, neutralization and washing stages can be substituted by a single filtration. In addition, selecting the most active and/or the most selective catalyst can increase the total yield of desired products and can also reduce by-products formation, thereby simplifying the distillation step. Besides, the heterogeneous catalysts are more easily separated from the reaction mixture and can be reutilized, so giving rise to more environmentally friendly processes.

Different groups have studied the heterogeneization of the aldol condensation of citral and acetone. Noda et al. [6] were the first to report the excellent performance of a Mg,Al-mixed oxide ($\text{Al}/(\text{Al} + \text{Mg}) = 0.27$) derived from hydrotalcite as a catalyst for this reaction under autogenous pressure, at 398 K with an acetone/citral molar ratio equal to 1 and a catalyst content of 10 wt.% (with respect to the total weight of reactants). After 4 h of reaction, a citral conversion of 98% was obtained with selectivity to pseudoionones close to 67%.

Recently, Mg,Al-mixed oxides with different compositions and physico-chemical properties obtained from hydrotalcites by thermal treatment at 723 K were evaluated at the same conditions as described above, using 5 wt.% of catalyst (with respect to the total weight of reactants) [7]. The results showed that the Mg,Al-mixed oxide derived from a hydrotalcite with an $\text{Al}/(\text{Al} + \text{Mg})$ ratio equal to 0.20 and aged at 333 K was the most active and selective catalyst. After 4 h of reaction, a PSI selectivity of 70% for a citral conversion close to 65% was obtained. These values are quite similar to those reported for homogeneous media.

Roelofs et al. [8,9] also studied this reaction using as catalyst a mixed hydroxide obtained from a hydrotalcite with

an $\text{Al}/(\text{Al} + \text{Mg})$ of 0.33, calcined under N_2 at 723 K and rehydrated at 303 K with decarbonated water [8]. For an acetone/citral molar ratio close to 250 and 1 wt.% of catalyst, a citral conversion of 65% and a PSI selectivity of 90% were obtained after 24 h at 273 K. The authors claim that the reaction is inhibited over this catalyst by higher concentrations of citral since no reaction was observed for an acetone/citral ratio of 20 even with 10 wt.% of catalyst. When the water in the pores of the rehydrated catalyst was replaced by ethanol, a higher activity was obtained (citral conversion of 92%), but the selectivity to PSI was lower (79%) [9]. At 296 K the selectivity to PSI was 87% for a citral conversion of 88%, after 24 h of reaction.

The aldol condensation between citral and acetone catalyzed by activated hydrotalcites ($\text{Al}/(\text{Al} + \text{Mg}) = 0.25$) was also evaluated by Climent et al. [10]. These authors showed that the inhibiting effect of citral on the catalytic activity reported by Roelofs et al. [8] can be avoided by increasing the reaction temperature from 273 to 333 K. Moreover, citral conversion and PSI selectivity were both favored by increasing the acetone/citral molar ratio and the reaction temperature, reaching 90% and 99%, respectively, after 4 h at 353 K with a ratio equal to 19 and 4.5 wt.% of catalyst. The rate of reaction was also improved by the direct addition of water (36 wt.%) to the freshly calcined hydrotalcite. For this rehydrated catalyst both citral conversion and selectivity of PSI equal to 99% were observed after 1 h of reaction at 333 K with acetone/citral molar ratio of 2.7 and 40 wt.% of catalyst.

As shown by different authors, the surface basic properties and consequently the catalytic performance of the mixed oxides derived from hydrotalcites depends on chemical composition, the optimum Mg/Al ratio depending on the basic site density and strength required to activate the reactant of the reaction under study [11,12–15]. As to the nature of the active basic sites, it is often accepted that in the case of Mg,Al-mixed oxides they are associated to hydroxide groups and different $\text{O}^{2-} - \text{Mg}^{2+}$ acid–base pairs [16,17]. Concerning the Lewis

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