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-cyclohexenil)-3-buten-2′-one) are products derived from essentials 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.
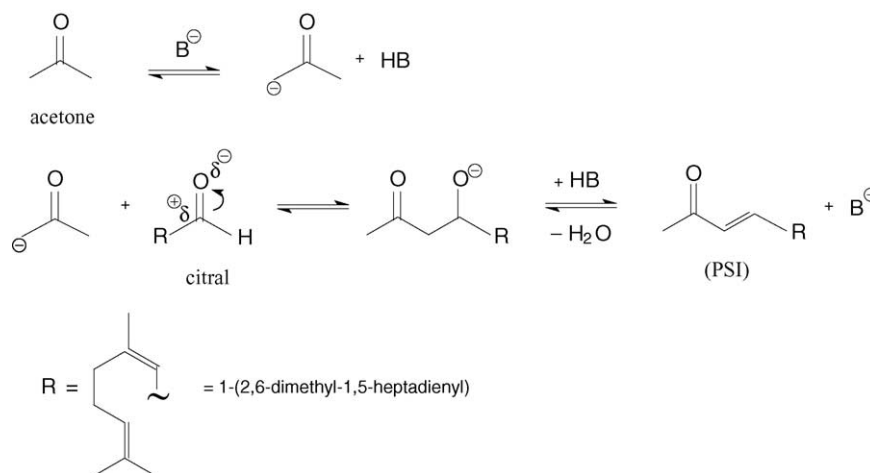
Fig. 1. Mechanism of aldol condensation between citral and acetone.

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 $(Al/(Al+Mg)=0.27)$ 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 $Al/(Al+Mg)$ 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 $Al/(Al+Mg)$ 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 $(Al/(Al+Mg)=0.25)$ 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 O^{2-}–Mg^{2+} acid–base pairs [16,17]. Concerning the Lewis

basic sites associated to O^{2-} anions, their basicity depends on their coordination. Those oxygen atoms located in the corner of the crystals (low coordination number) should have a stronger basicity than oxygen atoms located on the edges or on crystal faces [15,17]. On the other hand, the results of Guida et al. [18] suggest that the active sites for condensation reactions are mainly hydroxyl groups.

This work continues our systematic study of the first step of the ionone synthesis process, the production of pseudoionones by aldol condensation of citral and acetone over Mg,Al-mixed oxides as basic catalysts. The influence of acetone/citral molar ratio, temperature and reaction time on catalytic activity and selectivity was evaluated within ranges consistent with a commercial process. The Mg,Al-mixed oxide used as catalyst was that with the best catalytic performance in our previous work [7].

2. Experimental

2.1. Reagents

The citral used, containing 98 wt.% of the isomers geranial and neral, was purchased from Aldrich Co. Acetone (technical grade) was dried and distilled to reduce the water content to less than 0.07 wt.%.

2.2. Hydrotalcite synthesis

The hydrotalcite used as precursor was prepared by co-precipitation at 333 K, as previously described by Noda Pérez et al. [7]. An aqueous solution (solution A) containing $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (1.5 M in (Al + Mg) and with an Al/(Al + Mg) atomic ratio of 0.20) was slowly dropped under vigorous stirring on a highly basic carbonate solution (solution B), prepared by dissolving appropriate amounts of Na_2CO_3 and NaOH in distilled water to give $[CO_3^{2-}]$ equal to 1.0 M and a pH equal to 10 during the aging of the gel for 18 h. The solid obtained was then filtered and washed with distilled water (363 K) until pH 7.

To obtain the Mg–Al-mixed oxide the hydrotalcite sample was calcined under air from room temperature up to 723 K at 1 K/min and held at this temperature for 10 h.

2.3. Catalyst characterization

The chemical composition was determined by atomic absorption spectrometry (AAS) using a Perkin-Elmer AAS 1100B spectrometer. X-ray powder diffraction patterns of the samples were recorded in a Rigaku X-Ray generator equipped with a graphite monochromator using Cu Kα radiation, 40 kV and 40 mA. Thermal decomposition of the hydrotalcite sample was evaluated by TGA and DTA analyses carried out in a Rigaku Thermo balance TAS 100 under flow of air at 10 K/min up to 1273 K.

The textural characteristics (BET specific area, external area, microporous and mesoporous volumes) of the Mg,Al-mixed oxide were determined by N_2 adsorption–desorption at 77 K in an ASAP 2000 from Micromeritics.

2.4. Catalytic tests

The reaction was carried out in liquid phase employing a 50 ml stainless steel batch reactor magnetically stirred and heated in an oil bath. The active form of the catalyst was obtained by calcination ex situ under the conditions mentioned above (Section 2.2). After activation, it was rapidly transferred to the reactor containing the mixture of acetone and citral. The system was then heated up until the reaction temperature. The final temperature was always reached within less than 5 min from the addition of the catalyst.

Two methodologies were used to evaluate the influence of acetone/citral molar ratio (1, 5 and 10). In the first, a mass of catalyst corresponding to 7.16 wt.% of the mass of citral was employed whereas in the second the catalyst concentration was of 5 wt.% with respect to the total weight of reactants (for an acetone/citral molar ratio of 1 the two methodologies correspond to the same mass of catalyst). These tests were carried out at 398 K for 4 h under autogenous pressure, keeping constant the volume of the reaction mixture (12 ml).

Once the best acetone/citral molar ratio was defined, the catalytic tests for evaluating the effect of the temperature (343, 363, 383 and 398 K) and of the reaction time (30, 60, 120, 180 and 240 min) were carried out.

At the end of each test, the system was cooled down to room temperature and the phases separated by decantation. The liquid phase was analyzed by gas chromatography in a Chrompack 9001 chromatograph equipped with a 50 m Carbowax 20 M capillary column and FI detector. The samples were dissolved in *n*-hexane (technical grade) before the analysis. The reaction products were identified by gas chromatography-mass spectrometry in a GC–MS Shimatzu QP 2000A.

3. Results and discussion

3.1. Physico-chemical characterization

The chemical analysis of the hydrotalcite sample showed an Al/(Al + Mg) atomic ratio of 0.2, identical to that of the synthesis gel. This result associated to that of TGA/DTA indicated that the chemical formula of the sample was $Mg_{6.4}Al_{1.6}(CO_3)_{0.8}(OH)_{16} \cdot 6.4H_2O$.

The X-ray diffractogram of the synthesized sample indicated that diffraction lines corresponding to a hydromagnesite phase were also present besides the hydrotalcite pattern. The presence of a small quantity of a phase different from hydrotalcite was also observed by TGA/DTA and was associated to the high concentration of CO_3^{2-} and to the variation of the pH from 14 to 10 during the preparation of the gel [7].

The formation of magnesium hydroxycarbonate (hydromagnesite) along with hydrotalcite was also reported by Rey [19] for Al/(Al + Mg) molar ratios lower than 0.25 and pH lower than 11. As shown by Noda Pérez et al. [7], the presence of this small quantity of hydromagnesite did not influence the basic and the catalytic properties of the mixed oxide derived from this hydrotalcite sample.

Inspection of the N_2 adsorption/desorption isotherm of the Mg,Al-mixed oxide obtained by calcination of the hydrotalcite sample indicated a type IV (IUPAC) isotherm, associated to a mesoporous solid whose main textural characteristics were: $S_{BET} = 271\,m^2/g$, $S_{EXT} = 178\,m^2/g$ (t-plot method), $V_{MICRO} = 0.041\,cm^3/g$ (t-plot method) and $V_{MESO} = 0.60\,cm^3/g$ (BJH method).

More details on the physico-chemical characteristics of both the hydrotalcite precursor and the Mg,Al-mixed oxide were presented by Noda Pérez et al. [7].

3.2. Catalytic tests

In the present work, the citral purchased from Aldrich Co. (with 98 wt.% of citral isomers) substituted the Cuban lemongrass essential oil (91.3 wt.% of citral) used in the former studies [6,7]. The use of this more pure reactant decreased the formation of undesirable products, thus increasing both the citral conversion and the PSI selectivity as compared to those previously reported for the same catalyst on the same reaction conditions [7].

3.2.1. Acetone/citral molar ratio

Fig. 2 shows that the selectivity to pseudoionones was not significantly affected but that the citral conversion decreased when the acetone/citral molar ratio was raised. This result is in accordance with the first step of the aldol condensation mechanism shown in Fig. 1, in which the basic sites catalyze the formation of a carbanion by the abstraction of an α-proton from acetone. Increasing the amount of acetone in the reaction medium, while keeping it constant the amount of catalyst, reduces the catalyst/acetone ratio as the acetone/citral ratio is increased. As a consequence, the number of basic

sites is increasingly insufficient to abstract protons from the acetone molecules and the rate decreases. This suggests that the abstraction of the proton from the acetone molecule is the rate-limiting step of the reaction.

When the second approach was used (5 wt.% of catalyst as referred to the total weight of reactants), the citral conversion after 4 h at 398 K increased significantly (from 63 to 98%) whereas a slight increase in the PSI selectivity (from 74 to 78%) was observed when the acetone/citral molar ratio was increased from 1 to 5. The formation of a product resulting from the self-condensation of citral (PCS) was reduced significantly but the presence of products resulting from the condensation between pseudoionone and acetone molecules increases. So, an acetone/citral molar ratio of 5 and a catalyst content of 5 wt.% as referred to the total weight of reactants were selected to study the effects of temperature and reaction time.

3.2.2. Temperature and reaction time

The influence of temperature and reaction time on citral conversion and pseudoionone selectivity was evaluated in the range between 343 and 398 K with samples taken at 30, 60, 120, 180, and 240 min. In Fig. 3 one can observe that the conversion increases with increasing reaction temperature, as expected. A continuous increase in conversion is also observed with reaction time and an almost complete conversion of citral is attained after about 4 h for the tests at 383 and 398 K.

Fig. 4 shows the variation of PSI selectivity with citral conversion. For all temperatures the selectivity increased with increasing conversion. By reducing the temperature to 343 K, an important beneficial effect on PSI selectivity was observed when the results were compared at isoconversion, selectivities greater than 90% being achieved. The observed trends for the relationship between citral conversion and reaction time and between PSI selectivity and conversion suggest that better results can be obtained for reaction times longer than 4 h at 343 K. Moreover, these reaction conditions
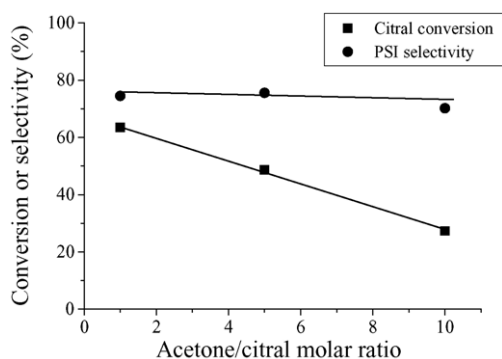

Fig. 2. Influence of acetone/citral molar ratio on citral conversion and PSI selectivity (7.16 wt.% of catalyst as referred to citral, 398 K, 4 h, autogenous pressure).
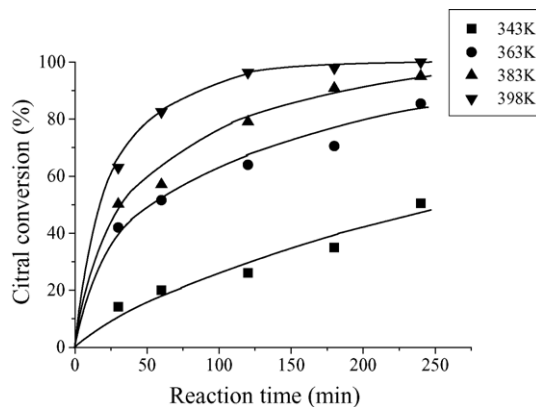

Fig. 3. Influence of temperature and reaction time on citral conversion (5 wt.% of catalyst as referred to the total weight of reactants, acetone/citral molar ratio = 5, autogenous pressure).
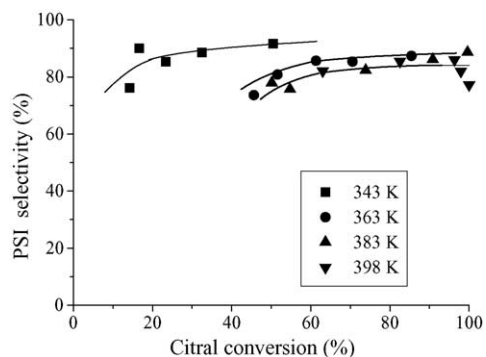
Fig. 4. PSI selectivity as a function of citral conversion (5 wt.% of catalyst as referred to the total weight of reactants, acetone/citral molar ratio = 5, autogenous pressure).

Table 1
Identification of the reaction products

Peak number	Substance
1 and 2	Citral isomers, geranial and neral
3 and 5	Main pseudoionone isomers (PSI_A and PSI_B)
4	Not identified
6–8	Pseudoionone isomers
9 and 10	Products derived from the condensation between a pseudoionone and an acetone molecule
11	Product derived from the self-condensation of citral (PCS)
12	Not identified

seem to be very adequate for the development of the process in a commercial scale.

Besides the pseudoionone isomers (products of interest) and the PCS (obtained from the self-condensation of citral), other by-products whose formation was influenced by acetone/citral molar ratio, temperature and reaction times were also detected. Aiming at elucidating the nature of these compounds, all the reaction products were analyzed by GC–MS.

3.3. GC–MS analyses

Fig. 5 shows the chromatogram for the products of the reaction carried out at 363 K, with acetone/citral molar ratio of 5, during 1 h. The correspondence between the peaks and the reaction products as identified by GC–MS is presented in Table 1. As can be observed, no products from the self-condensation of acetone were detected in these conditions.

For the reaction carried out at 363 K, a significant formation of the main reaction products, pseudoionone isomers (peaks 3, 5, 6, 7 and 8), can be observed along with the unreacted citral isomers (peaks 1 and 2) after 1 h. Isomers cor-
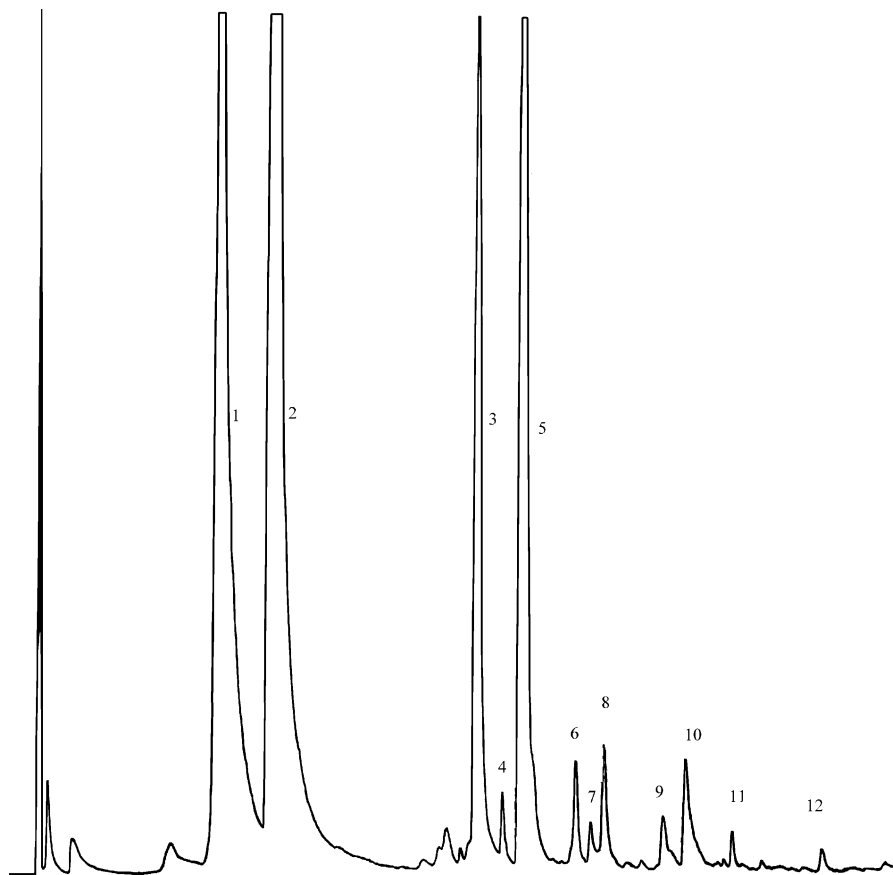

Fig. 5. GC-chromatogram obtained after 1 h for the reaction carried out at 363 K, 5 wt.% of catalyst (based on total weight of reactants) and acetone/citral molar ratio = 5.
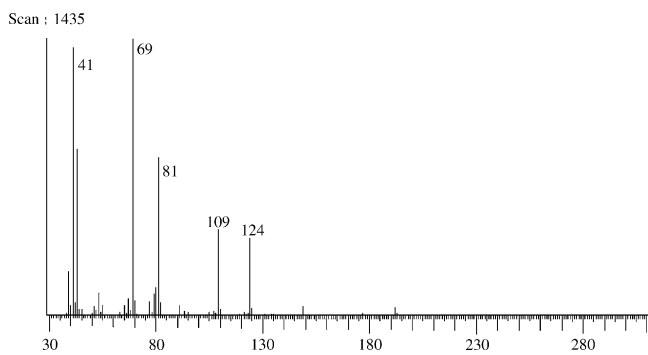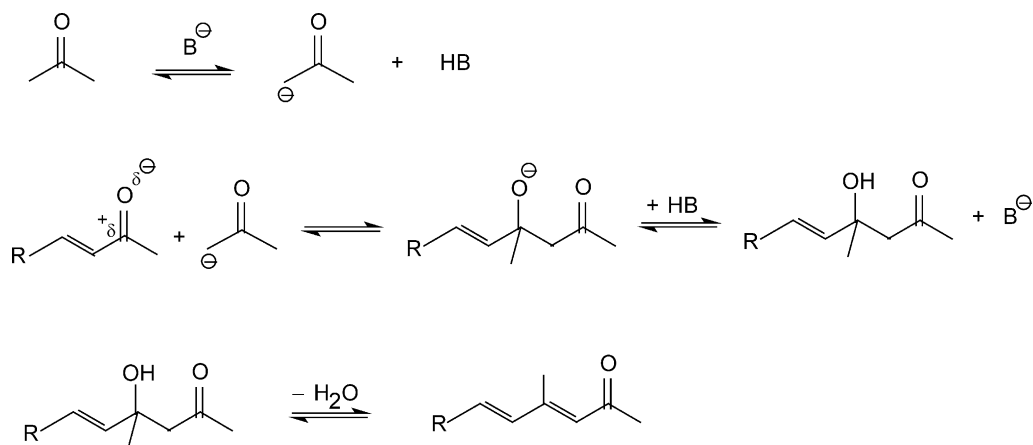
Scan : 1435

Fig. 6. Mass spectra of one of the pseudoionone isomers (peak 5 in Fig. 5).
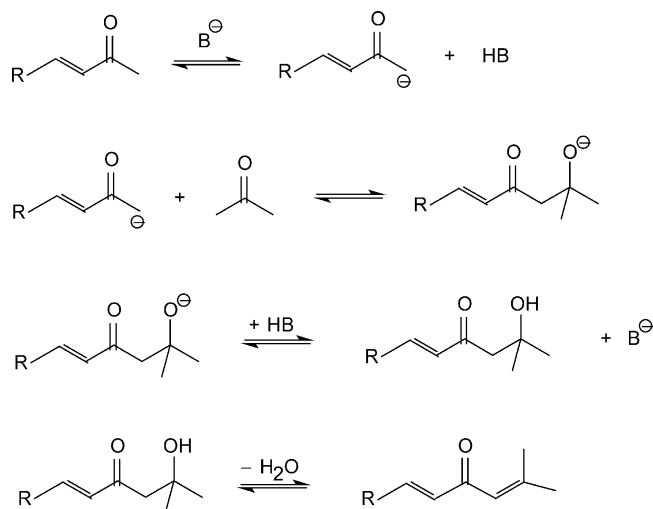
responding to peaks 6–8, which were favored by increasing the acetone/citral molar ratio from 1 to 5, practically disappeared with the increase in temperature and reaction time. Inspection of the mass spectra of the pseudoionone isomers, as illustrated in Fig. 6 for that corresponding to peak 5, indicates the presence of the following characteristic fragments: m/z 192, m/z 124, m/z 109, m/z 82, m/z 81, m/z 69 and m/z 41.

Products associated to peaks 9 and 10 were identified as deriving from the aldol condensation between a pseudoionone and an acetone molecule. For this reaction, the first step in the mechanism proposed in Fig. 7 is the formation of a carbanion from acetone (α-hydrogen abstraction), which attacks the carbonyl group of a pseudoionone molecule. An alternative mechanism is shown in Fig. 8. It involves the formation of a carbanion by the abstraction of an α-proton from pseudoionone and the subsequent attack to the carbonyl group of the acetone molecule. Mass spectra of products 9 and 10 (not shown) indicated the presence of the characteristic fragments: m/z 232, m/z 189, m/z 164, m/z 149, m/z 122, m/z 109, m/z 96, m/z 69 and m/z 41. The presence of the fragment $m/z = 189$ suggests

R = 1-(2,6-dimethyl-1,5-heptadienyl) (see Fig.1)

Fig. 8. Proposed mechanism for the aldol condensation between pseudoionone and acetone (abstraction of an α-proton from pseudoionone as the first step).

that the true reaction involves the formation of a carbanion from acetone, which is favored by an excess of acetone in the reaction medium. The formation of these products increases with the increase in both temperature and reaction time.

Finally, peak number 11 was confirmed to correspond to the product formed from the self-condensation of citral. This product was the only one observed when the reaction was carried out with only citral as reactant, at 398 K for 4 h.

From the complete identification of the reaction products a general route for the reaction between citral and acetone catalyzed by Mg,Al-mixed oxides can be proposed and is presented in Fig. 9.
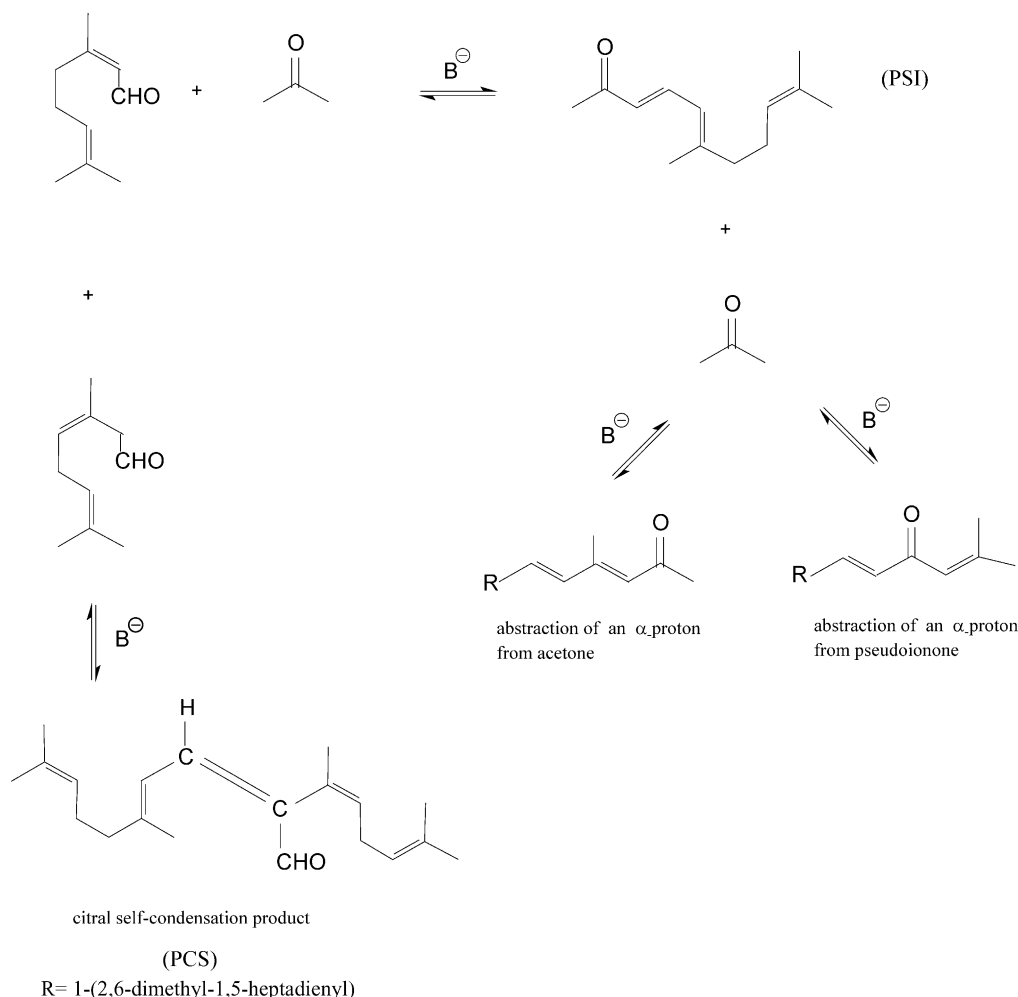

R = 1-(2,6-dimethyl-1,5-heptadienyl) (see Fig.1)

Fig. 7. Proposed mechanism for the aldol condensation between pseudoionone and acetone (abstraction of an α-proton from acetone as the first step).

Fig. 9. General scheme for the aldol condensation of citral and acetone over Mg,Al-mixed oxides in the experimental conditions studied in this work.

4. Conclusions

The Mg,Al-mixed oxide obtained by the thermal treatment of a hydrotalcite sample with an Al/(Al + Mg) molar ratio equal to 0.20 was confirmed as an active and selective catalyst for the production of pseudoionones from the aldol condensation of citral and acetone.

All reaction products were identified by GC–MS analyses and a general scheme for the reaction is proposed. Pseudoionone isomers were confirmed 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.

From the evaluation of the influence of several reactional parameters, the best reaction conditions for the production of pseudoionone with high selectivity (90%) were a temperature of 343 K, a catalyst concentration of 5 wt.% based in the total weight of reactants and an acetone/citral molar ratio of 5. The observed trends for the dependence of citral conversion with time and of pseudoionone selectivity with conversion suggest that for longer reaction times (>4 h) better results

on citral conversion and pseudoionone selectivity can be obtained. The suggested reaction conditions are appropriate for the development of the process in a commercial scale.

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