Synthesis of pseudoionones by acid and base solid catalysts

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Received 27 September 2001; accepted 3 January 2002

The preparation of pseudoionones by aldol condensation reaction between citral and acetone have been carried out in the presence of acid (HY and beta zeolites), an acid–base (amorphous aluminophosphate) and basic catalysts such as an aluminophosphate oxynitride, MgO and different activated hydrotalcites. The results showed that acid or acid–base catalysts were not successful for performing in one pot the preparation of ionones. MgO and calcined hydrotalcites showed excellent activity and selectivity to pseudoionones, with calcined hydrotalcite more selective than MgO. Moreover, the rate of reaction can be improved by activating the hydrotalcite through rehydration. This activation can be successfully done by simply adding the optimum amount of water to the calcined hydrotalcite before reaction. The inhibiting effect of the concentration citral on the catalytic activity of rehydrated hydrotalcites that has been reported to occur at 273 K can be avoided by working at a reaction temperature of 333 K.

KEY WORDS: solid base catalysts for pseudoionones; solid base catalysts for citral acetone condensation; solid base catalysts for adol condensation; hydrotalcites for condensation reactions.

1. Introduction

Aldol condensations are reactions directed to the formation of C–C bonds, and have numerous applications for the synthesis of pharmaceuticals [1], plasticizers [2] and fragrances [3].

Aldol condensation of citral with acetone or methyl ethyl ketone on basic catalyst and the subsequent cyclization of the acyclic precursors (called pseudoionones) over acid catalysts, form ionones and methylionones respectively of commercial interest [3]. Numerous commercial methods for the preparation of pseudoionones which are based on the aldolic condensation using conventional homogeneous catalysts such as aqueous alkali metal hydroxide solutions, alcoholates in alcohol or benzene as solvents, have been reported [4–7]. The yields of the cross-condensation compound obtained with these types of process are variable (between 50 and 80%) depending on the type of catalyst and the reaction conditions such as catalyst concentration, molar ratio of reagents and reaction temperature. Recently, because of the industrial importance of the process, there is interest in substituting conventional bases in homogeneous phase by heterogeneous catalysts such as alkali oxides, basic alumina and calcined hydrotalcites [8–10]. In this paper we describe the preparation of pseudoionones by aldol condensation reaction between citral and acetone (scheme 1) in the presence of acid, acid–base, or base catalysts such as beta zeolite, amorphous aluminophosphate (ALPO), aluminophosphate oxynitride, a high surface area MgO, and different activated hydrotalcites. These catalysts are easy to separate from the reaction media by filtering, avoiding the formation of by-products and the neutralization step, and moreover the unreacted ketone can be recovered in a substantial anhydrous state, thus facilitating recycle. As the reported rate of reaction in heterogeneous phase is too slow for industrial adaptation, a detailed study of the reaction conditions and the influence of the basic strength of the catalyst have been made in order to design a successful catalyst that allows production of pseudoionones with high conversion and selectivity.

2. Experimental

2.1. Materials

Beta zeolite (Si/Al = 13) was supplied by PQ Corporation in the acidic form. The USY sample was obtained from PQ Zeolites B.V. and calcined at 773 K for 3 h. The framework Si/Al ratio of USY zeolite was 30.

The amorphous aluminophosphate (AlPO) with a P/Al ratio of 1.0 was prepared following the method proposed by Lindblad *et al.* [11].

Nitridation procedure of the aluminophosphate was performed under ammonia flow (85 ml/min) at 1073 K for 10 h. At the end of the nitridation procedure the amount of nitrogen content was 6 wt% [12].

The MgO samples were prepared following the procedure previously reported [13].

Al-Mg hydrotalcites were prepared from gels produced by mixing two solutions, A and B. Solution A contains $(3-x)$ moles of $Mg(NO_3)_2 \cdot 6H_2O$ and x moles of $Al(NO_3)_3 \cdot 9H_2O$ in the $(Al+Mg)$ concentration

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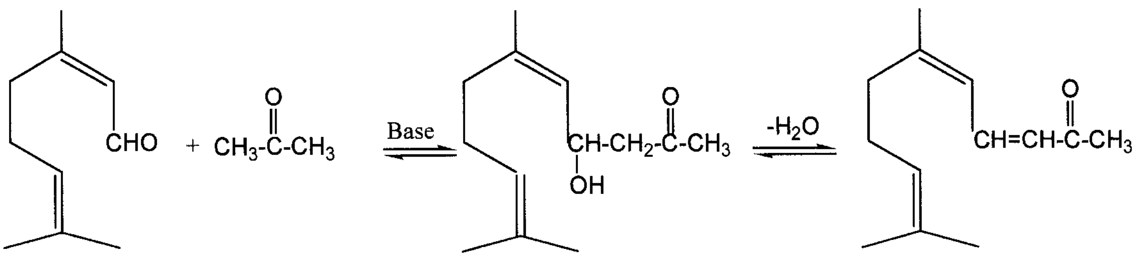

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Scheme 1.

of 1.5 mol/l for a range of Al/(Al + Mg) ratios between 0.20 to 0.33. Solution B is formed by $(6 + x)$ moles of NaOH and 2 moles of Na_2CO_3 dissolved in the same volume of the solution A. Both solutions were co-added at a rate of 1 ml/min under vigorous mechanical stirring at room temperature. The suspension was left for 12 h at 60 °C. The hydrotalcite was filtered and washed until pH = 7, and the solids were dried at 60 °C.

The hydrotalcite was activated by calcining at 723 K in a dry flow of N_2 (99.99). The temperature was raised at the rate of 2 °C/min to reach 723 K and maintained for 6 h. The solid was then cooled to room temperature. The calcined hydrotalcite (HTc) was rehydrated at room temperature under a flow of nitrogen saturated with water vapour free of CO_2. The flow of wet nitrogen (40 ml/min) was maintained for 24 h. In other experiments, hydrotalcites were rehydrated by direct water addition on the freshly calcined catalysts just before reaction.

The main characteristics of the hydrotalcite samples are summarized in table 1.

X-ray diffraction measurements were recorded with a Philips X'PERT (PN 3719) diffractometer (Cu K_α radiation provided by a graphite monochromator) equipped with an automatic variable divergence slit and working in the constant irradiated area mode.

Analyses of Mg and Al were performed using atomic adsorption. Infrared measurements were performed with a Nicolet 710 FT spectrophotometer using self supporting wafers of 10 mg cm^{-2} and a Pyrex vacuum IR cell. Prior to the collection of spectra the samples were heated in the cell for 2 h at increasing temperatures, after which the spectra were obtained at room temperature.

N_2 and Ar adsorption/desorption isotherms were performed at 77 and 87 K, respectively, in an ASAP 2010 apparatus from Micromeritics, after pretreating the samples under vacuum at 673 K overnight, and the BET surfaces were obtained using the BET methodology.

Table 1
Main characteristics of the catalysts

Catalyst	Al/Al + Mg	Surface (m^2/g)	Pore volume (cc/g)
ALPO	–	211	0.32
ALPON	–	210	–
HTc	0.25	227	0.87
MgO	–	246	0.61

2.2. Reaction procedure

Commercial citral, a mixture of *cis* and *trans* isomers (geranial and neral) with a proportion of 25 and 75 wt% respectively, was used without purification. Acetone (95.5% purity) was supplied by Aldrich.

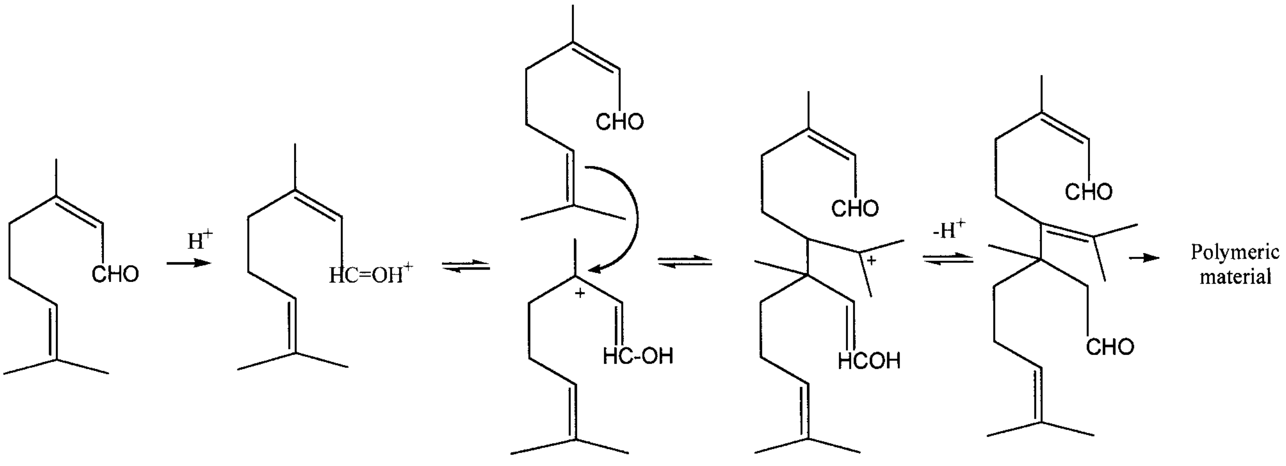
Typically, a mixture of citral (6.8 mmol), acetone (18 mmol) and the catalyst (414 mg) were added in a tree necked-bottom flask equipped with a condenser system. The resultant suspension was heated up to 333 K under vigorous stirring in an oil bath equipped with an automatic temperature control system. Samples were taken at regular time periods and analysed by gas chromatography (GC) using a FID detector and a Tracer-wax column (15 m × 0.32 mm × 0.25 μm). Nitrobenzene was used as internal standard. At the end of the reaction, after cooling, the reaction mixture was filtered to remove the catalyst. The response factors were calculated for each reactive agent from pure samples. Reaction products were identified by GC-MS (Hewlett-Packard 5988 A) and by ^{1}H-NMR spectroscopy (Varian VXR-400S, 400 MHz).

In another series of experiments the condensation reaction between citral and acetone was carried out using an autoclave system equipped with a mechanical stirring and automatic control of temperature and pressure. A solution of acetone (132 mmol, 7656 mg), citral (7 mmol, 1120 mg) and the catalyst (391 mg, 4.5 wt%) was added into the reactor, and it was heated up to 353 K for 4 h. At the end of the reaction, the catalyst was filtered, washed with acetone and the organic layer was analysed by GC-MS.

The ratio acetone/citral was modified by changing the amount of acetone and keeping constant the amount of citral and ratio citral/catalyst.

3. Results and discussion

It is known that aldol condensations can be catalysed by either acid or basic catalysts. In order to study the possibility of obtaining ionones in one pot by



Scheme 2.

heterogeneous acid catalysts, we started our study carrying out the condensation reaction between citral and acetone in the presence of two 12MR zeolites with different pore topology (HY and HB). However, when zeolites were used as catalysts the only products obtained were oligomers of the citral. In this case a protonation of the α,β-unsatured carbonyl system occurs, followed by alkylation of a second molecule of citral (scheme 2). When a bifunctional acid–base catalyst such as an amorphous aluminophosphate (ALPO) was used, a small amount of condensed product was detected, being in this case the dimerization of citral also the main process. If the same ALPO is treated at high temperature with NH_3, some isomorphic substitution of oxygen by nitrogen occurs in the solid (table 1) and an aluminophosphate oxynitride (ALPON) is obtained with formation of $-NH$ and/or $-NH_2$ groups that present a basic character [12]. When an ALPON with 6% N content was used as catalyst for the condensation of benzaldehyde with ethyl cyanoacetate the reaction proceeds very quickly, showing the basic character of this catalyst. However, when the aldol condensation between acetone and citral was carried out the activity of this catalyst is quite low. In a previous work we postulated that ALPONs were basic enough to abstract a proton from a reactant with a pK_a of 13. If we take into account that the pK_a of acetone is close to 20, we can explain the relatively low conversion obtained with this catalyst (see table 2).

From these results it seems that basic catalysts with strong basic sites would be more suitable to perform this condensation. At the laboratory scale, solid bases such as modified aluminas [10], alkaline exchanged zeolites [14], alkaline hearth oxides [14], alkali ion-modified alumina [14] and calcined hydrotalcites have been tested recently [15–17] as catalysts for aldol condensations.

In order to explore the influence of the basic strength of the catalyst on the aldol condensation of citral with acetone, we have chosen two solid catalysts that show strong Lewis basicity, *i.e.*, a mixed Al-Mg oxide derived from hydrotalcite (HTc), and MgO, which have shown activity and selectivity to catalyse aldol condensation reactions.

When the reaction was carried out in presence of these catalysts using an acetone/citral molar ratio of 2.7 at 333 K, the main products obtained were a mixture of *cis* and *trans* pseudoionone (6,10-dimethyl-3,5,9-undecatrien-2-one, **1**) (scheme 1). No β-hydroxyl ketone was detected under these conditions because of the facile dehydration of this compound to produce the α,β-unsaturated compound **1**, and the decrease of the equilibrium constant with temperature accounts for the difficulty in making aldols.

Other condensation products coming from the self-condensation of acetone, self-condensation of citral, and oligomers derived from citral were also detected in the reaction mixture.

Results from table 2 clearly indicate that the calcined Mg-Al hydrotalcite (HTc) and MgO show a larger catalytic activity than ALPO and ALPON, for carrying out the desired reaction. From table 2, it can be seen that MgO is able to achieve higher conversions than HTc; however, its selectivity is lower. The different

Table 2
Experimental results of the acetone with citral on different base catalysts [a]

Catalyst	Conversion of citral (%)	Yield of **1** (%)	Others (%)	Selectivity of **1** (%)
HTc	35	18	17	51
	64	46	18	72
	86 [b]	68	18	79
MgO	64	34	30	53
	92	61	31	66
	99 [b]	68	31	68
ALPO	6 [b]	1	5	16
ALPON	10 [b]	1	9	10

[a] Reaction conditions: acetone/citral molar ratio of 2.7; catalyst 16.6 wt% at 333 K.

[b] 1 h reaction time.

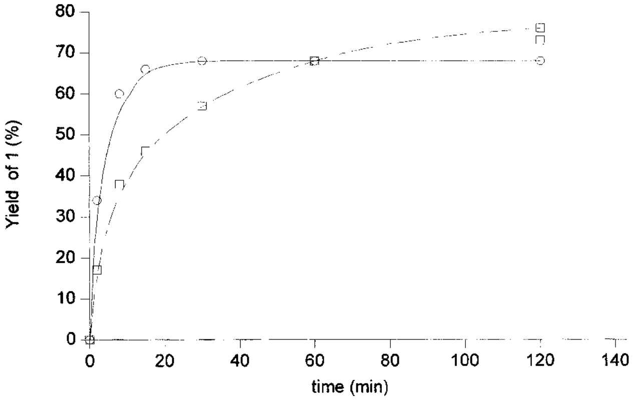


Figure 1. Yields of pseudoionone *versus* time obtained in the reaction between acetone and citral using an acetone/citral molar ratio of 2.7 at 333 K, in presence of MgO (○) and calcined hydrotalcite (□).

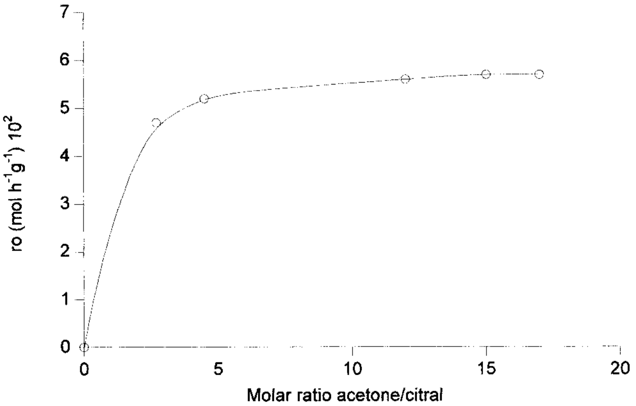


Figure 2. Influence of the acetone/citral molar ratio on the initial rate (mol h^{-1} g^{-1}) of formation of pseudoionone at 333 K in the presence of calcined hydrotalcite (40 wt/wt% with respect to citral).

activity of MgO and HTc is better seen in figure 1 where the yields of pseudoionone *versus* time for both catalysts are plotted. MgO exhibits higher activity than HTc at short reaction times, probably due to the higher density of the basic sites existing on the surface of the former. However, at longer reaction times, HTc achieves a higher yield and selectivity of **1**. Owing to the better selectivity exhibited by HTc we selected this solid as catalyst to optimize the reaction conditions to form the pseudoionone.

3.1. *Influence of the acetone/citral ratio and reaction temperature*

It has been recently shown [9] that rehydrated hydrotalcites were very active for the condensation of acetone and citral at temperatures of 273 K. The authors found that with a molar acetone/citral ratio of 20 (10 wt% of citral) the desired condensation reaction did not take place while, when the amount of citral was decreased to 1 wt%, both acetone self-condensation and citral–acetone condensation occurred. The authors claimed that a negative reaction order in citral takes place, and the inhibition of citral could be due to a strong adsorption of citral on the catalyst surface. If this is true, and taking into account that the adsorption is exothermic, the inhibition should decrease when working at a higher reaction temperature. In order to test this, the reaction was carried out at 333 K in presence of HTc and using acetone/citral molar ratios of 2.7, 4.5, 12, 15 and 17 mol mol^{-1} (40% (wt/wt) of catalyst respect to citral). In figure 2 the initial rate of formation of **1** *versus* the acetone/citral molar ratio is displayed, and shows that the rate of pseudoionone formation increases when the acetone/citral molar ratio increases up to a value of 4.5 from which the ratio of reagents have little influence on the initial activity. Concerning the influence of the molar ratio of reagents on the yield and selectivity of **1**, the results from table 3 suggest that working at molar ratios higher than 4, it is possible to achieve after 1 h reaction time a good conversion of citral with selectivities to pseudoionone of 90–99%. The increase of selectivity when increasing the acetone/citral ratio can be due to the decrease in concentration of citral that will diminish the rate of oligomerization of this reagent. No improvements of yield and selectivity of **1** were observed at longer reaction times. These results clearly show the possibility of achieving higher conversions and selectivities at much lower acetone/citral ratios than those obtained before [9], by using a less active catalyst but working at 333 K instead of 273 K.

A higher reaction temperature (353 K) was explored by performing the reaction in an autoclave system, in the presence of MgO and HTc, and using an acetone/citral molar ratio of 19. After 4 h of reaction time the same conversion was obtained with both catalysts (90%). Nevertheless, a yield of 90% of pseudoionone with a selectivity of 99% was observed on HTc, whereas in the case of MgO lower yield and selectivity were reached (see table 3). In this case others by-products coming from the self-condensation of citral were also

Table 3
Results of the aldol condensation between acetone and citral using different reactant ratio and reaction temperature[a]

Catalysts	Acetone/citral molar ratio	*T* (K)	Conversion of citral (%)	Yield **1** (%)	Selectivity **1** (%)
HTc	2.7	333	86	68	79
	4.5	333	90	85	92
	12	333	89	75	84
	15	333	84	80	95
	17	333	83	83	99
HTc	19	353	90[b]	89	99
MgO	19	353	90[b]	69	77
ALPO	19	353	25[b]	6	25

[a] Reaction conditions: at 1 h reaction time, using 40 wt% of the catalyst with respect to citral.

[b] At 4 h reaction time, in autoclave system.

detected. If we compare these results with those obtained at 333 K, we can conclude that by increasing the reaction temperature by 20 K it is possible to achieve an excellent conversion and selectivity to pseudoionone using calcined hydrotalcite as catalyst, and in any case much higher than when working at 273 K on the hydrated hydrotalcite [9].

3.2. Influence of the pre-treatment of hydrotalcite on catalytic activity

At this point, we concentrated our attention on the most active catalyst found in this study, i.e. hydrotalcite. Hydrotalcites are Mg-Al hydroxycarbonates with laminar structure. The isomorphic substitution of Mg^{2+} by Al^{3+} produces layers with an excess of positive charges which are compensated by carbonate anions located in the interlamellar space. Thermal decomposition above 723 K results in the formation of a highly active homogeneous mixed oxide which is potentially a basic catalyst for a variety of organic transformations such as self-condensation of acetone [18] and the condensation of formaldehyde and acetone [19]. Recently, it has been shown that the calcined product can be activated by rehydration at room temperature by contacting with a stream of nitrogen saturated with water vapour during long periods of time [17]. It is a general belief that the basic sites produced by calcination are oxygen anions of low coordination, which correspond to Lewis basic sites, and when the hydrotalcite is rehydrated these basic sites are converted to hydroxyls or basic Brønsted sites which became the compensating interlayer anions.

In order to study the influence of activation by rehydration of HTc on the catalytic activity, the aldolization of citral with acetone was carried out at 333 K in the presence of two hydrotalcite samples, one just calcined and another calcined and then rehydrated for 24 h using a CO_2 free flow of nitrogen saturated with water.

The X-ray diffraction of the materials is displayed in figure 3. After calcination at 723 K their structure is that of a mixed Al_2O_3-MgO oxide, while after rehydration the original laminar structure was partially recovered. With respect to the catalytic activity, the results presented in figure 4 show that the rehydrated hydrotalcite is more active and selective than the calcined sample, it being possible to achieve 95% yields of pseudoionone with a selectivity of 99% after 1 h reaction time. These results are in good agreement with those reported previously [17].

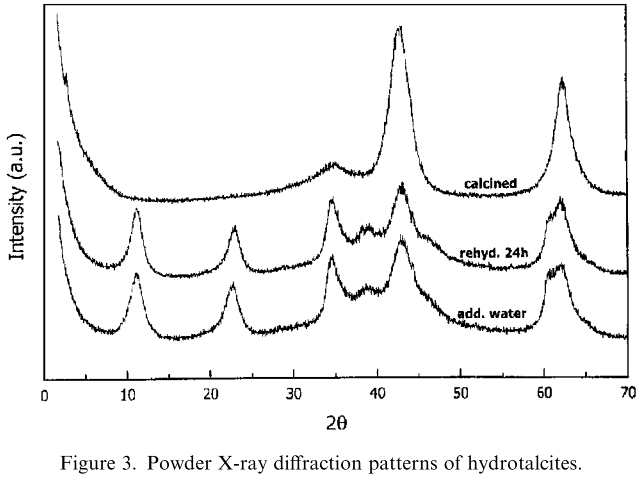


Figure 3. Powder X-ray diffraction patterns of hydrotalcites.

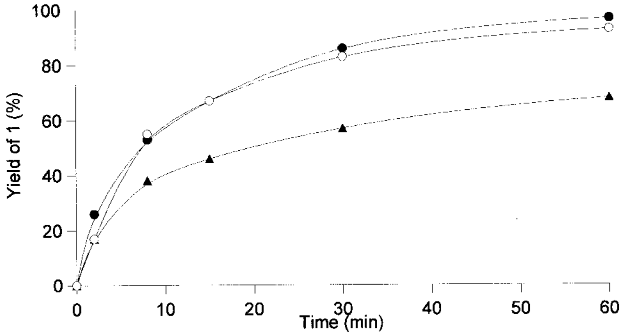


Figure 4. Results of aldol condensation between acetone and citral molar ratio of 2.7 at 333 K, in the presence of calcined hydrotalcite (▲), 24 h rehydrated (36% of water) (●) and with a 36% of water added (○).

3.3. Influence of the water content of the catalyst on the reaction rate

It has been reported [9] from CO_2 adsorption measurements that only 5% of the total available basic sites in the rehydrated HTc participate in the condensation reactions, and these sites are most likely localized at the edges of HT platelets. At this point we thought that the more accessible basic sites could be activated in a similar way by adding water directly on fresh calcined HTc, avoiding in this way the tedious and time-consuming rehydration procedure reported and which involves a stream of nitrogen saturated with water. Meanwhile, there is the possibility that the heat liberated by the fast rehydration of the oxides may cause breaking of particles, increasing in this way the number of accessible OH basic sites. In order to study this, the condensation reaction was performed adding previously on the calcined hydrotalcite the same amount of water as introduced during the 24 h rehydration treatment done previously. A comparison (figure 4) between the previous samples (calcined hydrotalcite (HTc), rehydrated (HTr) (36 wt%, water respect to solid catalyst) and water added hydrotalcite (HTa) (150 μl which corresponds to 36 wt% of water), showed that the calcined HT was much less active than the rehydrated samples. However, HTr sample presents practically the same activity as the HTa sample.

The role of the water in the catalytic process is complex since it reacts with the solid to produce Brønsted basic sites and it is also one of the reaction products. Then, considering that aldol condensation is a reversible reaction, one should be careful about the amount of

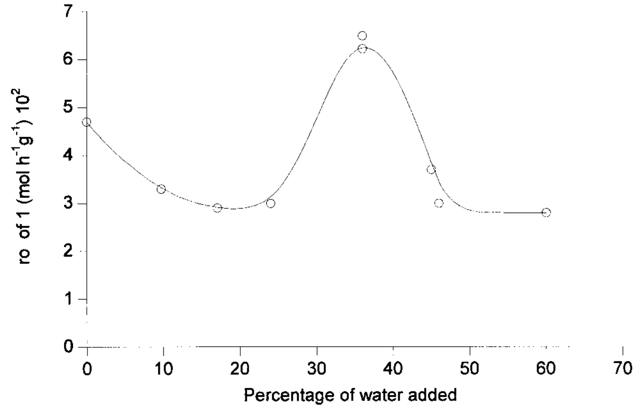


Figure 5. Influence of the water content of hydrotalcite on the initial rate (mol h^{-1} g^{-1}) of formation of pseudoionone at 333 K.

water added, since an excess of water over the HTc catalyst should shift the reaction equilibrium towards the formation of citral. Therefore it should be expected that a maximum of activity should occur for an optimum amount of water added on the catalyst. In order to study this parameter we have carried out the condensation reaction adding different percentages of water directly on HTc. In figure 5 we can see the variation of initial rate as a function of the amount of water added on the freshly calcined HT. It can be seen there that the activity goes through a maximum obtained for 150 μl water added (36% water). Note the narrow window which exists for achieving the desired catalytic effect. Curves with similar shape were encountered in aldol condensations using ethanol with different amounts of water content as solvent [16].

At this point it is clear that after rehydration one has a catalyst with different activity/adsorption properties, and consequently the influence of the acetone/citral ratio should again be explored on this catalyst. Then, the condensation was carried out using HTc with an amount of water added of 36 wt% and working at different acetone/citral molar ratios. Figure 6 shows that the rehydrated hydrotalcite does not follow the same behaviour as the calcined hydrotalcite with respect to the ratio of acetone/citral in the reaction media. In the case of the rehydrated hydrotalcite a maximum in conversion and selectivity is obtained for acetone/citral ratio between 2.7 and 4.6 mol mol^{-1} (see table 4). After this, a decrease of the catalyst activity is observed when further increasing the acetone/citral ratio, indicating that the nature and distribution of basic sites in the rehydrated catalyst has a strong influence on the kinetic behaviour of the reaction and hence on the final yield and selectivity of pseudoionone. In table 4, we can see that working at low molar ratios of reagents (2.4) it is possible to achieve, after 1 h reaction time, yields of pseudoionone higher than 90% with selectivities close to 100%, whereas an increase in the acetone/citral has little influence on the selectivity to **1**, in clear contrast to the results obtained on calcined HT (see table 3).

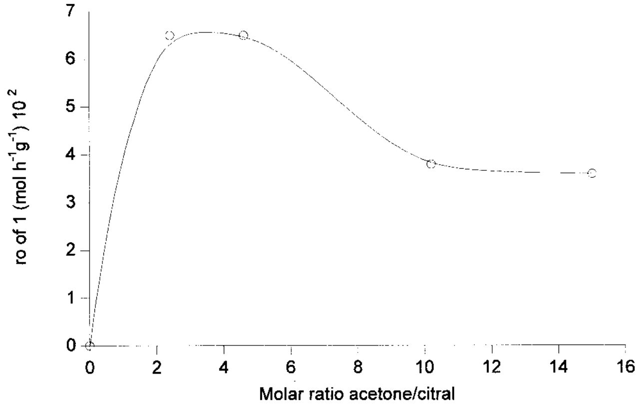


Figure 6. Influence of the acetone/citral molar ratio on the initial rate (mol h^{-1} g^{-1}) of formation of pseudoionone at 333 K in the presence of hydrotalcite with a 36% water content.

Table 4
Results of reaction of acetone with citral in the presence of HTc with water added of 36 wt% at 333 K using different acetone/citral ratio[a]

Acetone/citral molar ratio	Conversion of citral (%)	Yield of **1** (%)	Selectivity of **1** (%)
2.7	99	98	99
2.7	96	91	95
4.4	98	95	97
4.6	96	91	95
10.2	86	85	98
15	83	72	87

[a] Results obtained at 1 h reaction time using 40 wt% of the catalyst with respect to citral.

4. Conclusions

We have found that by working at temperatures of 333 K it is possible to avoid the inhibiting effect of citral, that has been reported to occur at 273 K, allowing the condensation reaction of acetone with citral to be carried out with excellent conversions and selectivities with relatively low acetone to citral ratios.

While calcined hydrotalcites already perform this reaction very well, the rate of the reaction can be improved by rehydrating the calcined hydrotalcite as was previously found by others [17]. However, the optimum catalyst can be obtained by directly adding the water on the calcined hydrotalcite (36 wt% water), and a long (24 h) rehydratation treatment by water in a nitrogen stream is not required. Owing to basicity/adsorption differences between calcined and rehydrated hydrotalcite, a different behaviour of reaction rate and selectivity to the desired product *versus* acetone/citral ratio is observed, which should be attributed to the different nature and distribution of basic sites existing for both samples.

The inhibiting effect of citral on the catalytic activity of rehydrated hydrotalcites has been avoided by working with calcined hydrotalcites at 333 K reaction temperature. Under these conditions high activities and selectivities can be obtained at short reaction times. Finally, acid or acid–base catalysts were not successful for producing the ionones in one pot.

Acknowledgments

The authors thank Comisión Interministerial de Ciencia y Tecnología (CICYT) (MAT2000-1392) for financial support.

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