# Condensation of citral and ketones using activated hydrotalcite catalysts

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Activated hydrotalcite catalysts were prepared *via* calcination and room-temperature rehydration. Replacement of water from the pores after rehydration resulted in an increased amount of accessible active sites. The performance of the catalyst was explored in liquid-phase aldol condensations at low temperatures. In the citral–acetone condensation high activities and selectivities were obtained. Usage in the citral–MEK condensation showed also a high citral conversion, with methyl pseudoionones as primary products.

**KEY WORDS:** hydrotalcite; solid-base catalysts; citral; aldol condensation; (methyl) pseudoionones

## 1. Introduction

Citral is a key starting material for various fine chemical products, in particular for the synthesis of several types of pseudoionones (PS). PS is an intermediate in the commercial production of vitamin A and is synthesised *via* condensation of citral and acetone. Citral consists of two isomers, neral and geranial, caused by the *cis*–*trans* isomerism at the C=C bond near the aldehyde group. Natural resources are several Indian lemon grass species and *Litsea cubeba* oil from the PR China, the latter source having a citral content as high as 75% [1]. When MEK is used instead of acetone, the base-catalysed formation of two different carbanions results in *n*-methyl and isomethyl PS [2] (shown in figure 1). After an additional acid-catalysed ring closure using strong acids like sulphuric and phosphoric acid, (methyl) ionones are obtained [2,3]. The production of ionones and methyl ionones, large-scale products in the flavours and fragrances industry, was estimated in 1995 at 3500 tonnes [4]. In the commercial production processes NaOH or KOH are used as homogeneous catalysts, which leads to waste streams [2,5]. Besides environmental problems concerning the use of alkali bases, the condensation of citral with ketones suffers from undesired side reactions, *e.g.*, citral self-condensation and secondary reactions of PS [6]. In recent years, a growing interest has developed in the utilisation of solid catalysts in base-catalysed reactions, especially in liquid-phase aldol condensations at low temperatures. Diacetone alcohol (DAA) production via self-condensation of acetone [7,8] and the benzaldehyde condensation with acetone towards benzalacetone [9] using activated hydrotalcite-based catalysts are noteworthy examples thereof.

Hydrotalcites (HTs) are anionic clays, the structure of which resembles that of brucite, $Mg(OH)_2$. In the latter structure, magnesium cations are octahedrally coordinated by hydroxyl ions, giving rise to a stack of layers of edge-shared octahedra. In HT, part of the $Mg^{2+}$ ions is replaced by $Al^{3+}$ ions resulting in positively charged cation layers, which charge is compensated by anions (usually carbonate). Besides anions, also water molecules are present in the interlayer [10–12].

To obtain activity in liquid-phase aldol condensations, HT has to be activated in a two-step activation procedure. First, by calcination up to 723–773 K, interlayer carbonate is removed and the layered HT structure is destroyed due to cation-layer dehydroxylation [10]. The resulting mixed oxides exhibit strong Lewis basicity as well as acidity and have been applied as a base catalyst in various gas-phase condensation reactions [13,14]. However, usage of calcined HTs in liquid-phase systems at low temperatures has not been very successful [15], possibly due to the presence of strong Lewis base sites [16]. The second activation step involves rehydration at room temperature. This results in the recovery of the original layered structure, but now with the required Brønsted base hydroxyl ions present in the interlayer. The thus obtained activated HT catalyst shows high activity and selectivity in several condensation reactions [9,17].

Recently, we succeeded in the condensation of citral and acetone to PS already at 273 K using the activated HT catalyst [18]. In this paper, we present supplementary and new results from the citral–acetone condensation as well as new results from the condensation reaction of citral and MEK towards methyl PS using HT-based catalysts. Furthermore, the activation procedure has been modified leading to a considerably enhanced number of active sites.

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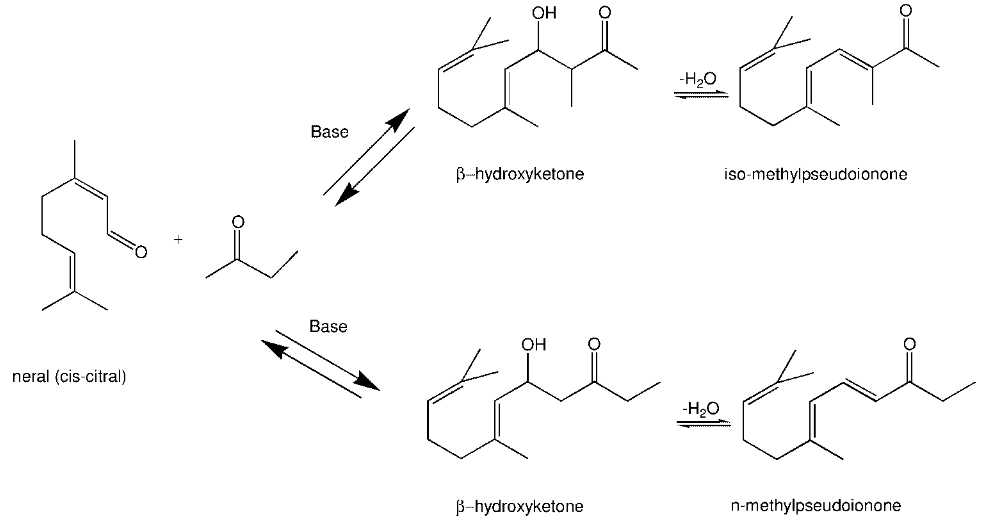

Figure 1. Base-catalysed condensation of citral and MEK yielding *n*-methyl and isomethyl pseudoionones *via* the $\beta$-hydroxy-ketone intermediate.

## 2. Experimental

### 2.1. Preparation of the catalyst

An aqueous solution (45 ml) of 0.1 mol $Mg(NO_3)_2\cdot 6H_2O$ and 0.05 mol $Al(NO_3)_3\cdot 9H_2O$ was added all at once to a second solution (70 ml) containing 0.35 mol NaOH and 0.09 mol $Na_2CO_3$ at 333 K. The mixture was maintained at this temperature for 24 h under vigorous stirring, after which the white precipitate was filtered off and washed several times. Drying of the hydrotalcite took place for an additional 24 h at 393 K. Using results from EDAX measurements, an Mg/Al ratio of 2/1 was calculated. Combined with TG-analysis results, the HT structure $Mg_6Al_3(OH)_{18}(CO_3)_{1.5}\cdot 4H_2O$ was derived.

After drying, the HT was heated in a nitrogen flow up to 723 K with a heating rate of 10 K/min and kept at this temperature for 8 h. Samples of the calcined HT were immersed in $CO_2$-free water (100 ml/g) and stirred under nitrogen atmosphere for 1 h at room temperature. After filtration under nitrogen atmosphere, some samples were subjected to an extra washing step using ethanol. All samples were dried under a nitrogen flow at room temperature.

### 2.2. Reaction procedures

The condensation reactions of citral with acetone or MEK were performed in a stirred double-walled thermostatic glass reactor, equipped with baffles. To suppress self-condensation of citral, a high ketone/citral ratio was applied. Typically, 145 ml ketone containing 1 wt% citral (95%, Aldrich) was cooled to 273 K and 0.5 g freshly prepared catalyst was added under a low flow of nitrogen to exclude atmospheric carbon dioxide. Aliquots of 1 ml were taken from the reaction mixture during the 24 h reaction period and analyzed using a Chrompack CP 9001 GC provided with a Chrompack CP 9050 autosampler. Tetradecane (99%) was used as internal standard to calculate the amount of citral and, in case of the citral–acetone condensation, the amount of PS formed. The selectivity has been calculated by using both the $\beta$-hydroxy-ketone and PS signals from the GC analysis. In case of the self-condensation of acetone, isooctane was used as internal standard to calculate the amount of DAA formed.

#### 2.2.1. Catalyst characterisation

Powder X-ray diffraction (XRD) patterns were obtained by using an Enraf Nonius FR 590 with Co K$\alpha$ radiation. A Micromeritics ASAP 2400 analyzer was used for $N_2$ physisorption to determine surface areas and pore volumes. Volumetric $CO_2$-adsorption measurements in the pressure range 0–1 mbar were performed at 273 K using a Micromeritics ASAP 2000. After calcination and/or rehydration as described above, the samples were stored under nitrogen to avoid $CO_2$ uptake from the atmosphere. Before characterisation measurements were performed, the samples were outgassed under vacuum at 393 K.

## 3. Results and discussion

The XRD patterns of the HT at different stages of activation are depicted in figure 2. The diffraction pattern of the HT as synthesised ($HT_{as}$) shows the characteristics of a highly crystalline layered structure and is analogous with HTs reported in literature [10,19]. Calcination of the HT up to 723 K resulted in the disappearance of the layered structure, as can be concluded from the absence of the $00l$ signals in figure 2(b). The broadened MgO-like signals point to the formation of a mixed oxide of the Mg(Al)O type [10]. After rehydration of the calcined HT at room temperature the restoration of the original layered structure had occurred (figure 2(c)). Although this compound is less crystalline than the $HT_{as}$, the typical HT characteristics can clearly be recognized. Earlier XANES results showed a complete return of the octahedral coordination of the Al ions present in the cation layer after rehydration [20], using this procedure.

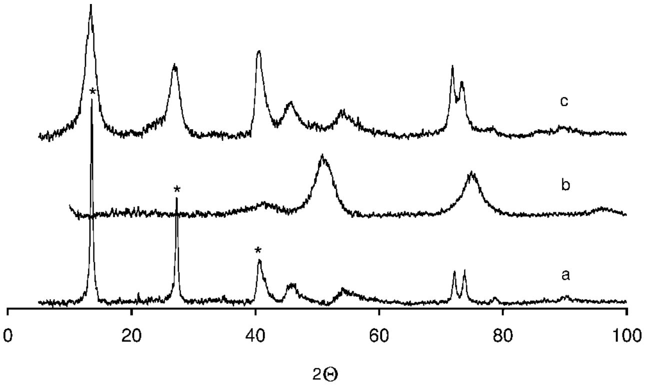

Figure 2. X-ray diffraction patterns of (a) HT as synthesised, (b) HT calcined and (c) HT after rehydration.

Table 1
Results from physisorption and catalytic measurements.

| | BET surface area ($m^2$/g) | Micropore volume (ml/g) | Total pore volume (ml/g) | $CO_2$ adsorption (ml STP/g) | Activity[a] ($g_{DAA}/g_{cat}$ h) |
|---|---|---|---|---|---|
| $HT_{as}$ | 100 | 0.00 | 0.76 | n.d. | 0 [17] |
| $HT_{calc}$ | 224 | 0.03 | 0.87 | n.d. | 2 [17] |
| $H_{act}$ | 97 | 0.00 | 0.44 | 3.8 | 15 |
| $HT_{act,w}$ | 200 | 0.00 | 0.49 | 6.2 | 28[b] |

[a] Initial activity in acetone self-condensation at 273 K, reaction conditions similar to those of [17].

[b] Reaction temperature 296 K.

Table 1 shows the results from physisorption measurements. Calcination of the HT resulted in a large increase in BET surface area from 100 to 224 $m^2$/g, due to the formation of micropores as well as of mesopores [13]. The micropores vanished during rehydration while the layerered structure restored resulting in a significant decrease of the BET surface area, from 224 to 97 $m^2$/g for the dried rehydrated HT ($HT_{act}$) caused by both the closure of micropores within platelets and the agglomeration of platelets closing mesopores. The latter phenomenon results from the high capillary forces excited by the withdrawing water menisci between the HT platelets during drying. Replacement of water by ethanol followed by drying causes the capillary forces to be substantially lower such that the high specific surface area can be maintained (table 1). Furthermore, results from $CO_2$-adsorption measurements executed at low pressures show a significantly higher uptake of $CO_2$ on the washed activated HT ($HT_{act,w}$) than on the $HT_{act}$. Washing with ethanol enhanced the number of Brønsted sites as well as the activity for acetone condensation approximately two fold (table 1).

The $HT_{act,w}$ was used in our citral–ketone catalysis experiments. Previous results with the $HT_{act}$ [18] showed that using a molar acetone/citral ratio of 20 (corresponding to 10 wt% of citral), no reaction took place at all. When the amount of citral was decreased to 1 wt%, both acetone self-condensation and citral–acetone condensation was observed (65% citral conversion after 24 h, 90% selectivity towards PS). This demonstrates a strong inhibition by citral at higher concentrations of citral. Therefore, all experiments with the $HT_{act,w}$ were performed with a starting concentration of 1 wt% citral.

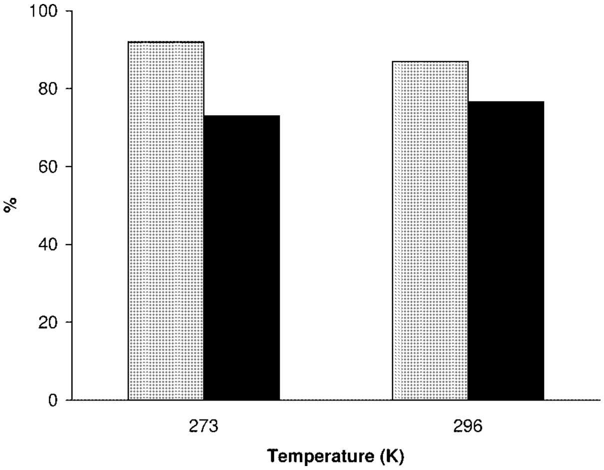

Figure 3. Citral conversion (%) (□) and PS yield (%) (■) at 273 and 296 K in the citral–acetone condensation.

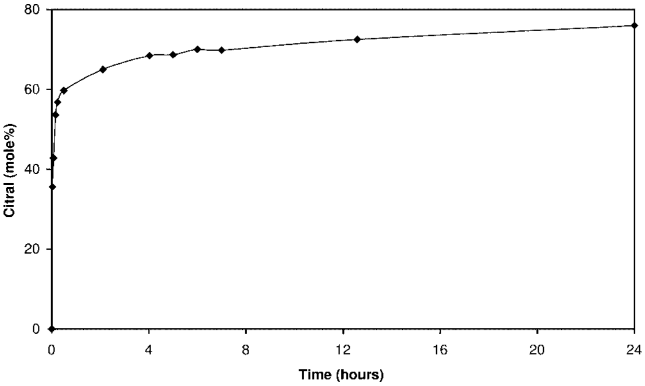

Figure 4. Conversion of citral in the citral–MEK condensation at 296 K.

First, the catalytic performance of the $HT_{act,w}$ was tested in the citral–acetone condensation at 273 K. Figure 3 shows the conversion of citral at 273 K and the formation of combined PS and $\beta$-hydroxy ketone. After 24 h, a conversion of 92% citral was found, which is significantly higher than the earlier reported 65% of the $HT_{act}$. The selectivity, however, is somewhat lower (79 *versus* 90%), possibly due to an increased adsorption of citral on the $HT_{act,w}$ catalyst. This hypothesis is supported by the observed fast, almost instant citral removal after short reaction times (figure 4). To examine the effect of temperature on the $HT_{act,w}$ performance, the condensation reaction was carried out at 296 K. Citral conversion and PS formation are depicted in figure 3 also. A slightly increased selectivity towards PS was observed at this higher temperature, 87%, and a citral conversion of 88% was achieved. Besides PS also DAA, as a result of acetone self-condensation, was observed at both temperatures. Thermodynamic equilibrium (23 and 13 wt% DAA at 273 and 296 K, respectively [21]) was not reached, possibly due to catalyst deactivation. Interestingly, the presence of citral gave rise to the formation of ~2 wt% of triacetone alco-

Table 2
Citral–ketone catalysis results.

| Catalyst | Temperature (K) | Ketone | Initial activity ($g_{citral}/g_{cat}$ h) | Selectivity (mol%) |
|---|---|---|---|---|
| $HT_{act}$[a] | 273 | Acetone | 1 | 90 |
| $HT_{act,w}$ | 273 | Acetone | 2 | 79 |
| $HT_{act,w}$ | 296 | Acetone | 2 | 87 |
| $HT_{act,w}$ | 296 | MEK | 1 | n.d. |

[a] Data from [17].

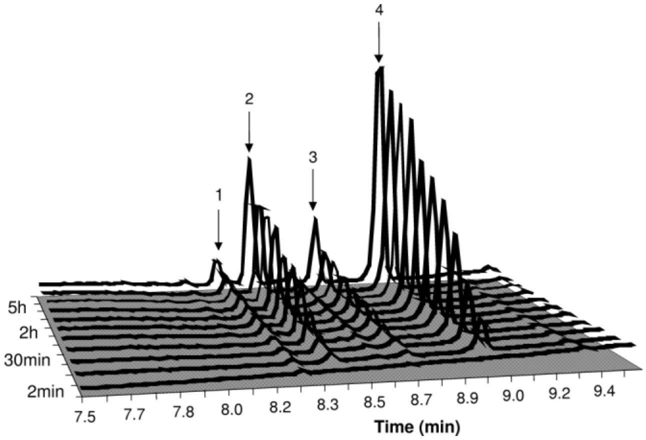

Figure 5. GC chromatograph showing the formation in time of the desired methyl-PS products (1 and 2 iso- and $n$-methyl PS from neral, 3 and 4 iso- and $n$-methyl PS from geranial, respectively).

hol, a higher condensation product of acetone, which formation was not observed during tests in the self-condensation of acetone under similar conditions (table 1 and [18]). Moreover, it appears from the quantitative initial rate data (tables 1 and 2) that the $HT_{act,w}$ is twice as active as the $HT_{act}$, whereas the increase in temperature did not result in a further activity increase.

Figure 4 shows the results of the citral MEK condensation experiments at 296 K using the $HT_{act,w}$. A conversion level of 76% after 24 h was obtained. Obviously, the formation of two different carbanions occurs resulting in a redoubling of the possible products. With the two isomers of citral and the redoubling of the $\beta$-hydroxy-ketone intermediates, eight products can be expected (figure 1). Under the applied analysis conditions, separation of the methyl PS and the corresponding $\beta$-hydroxy-ketone intermediate did not occur. We have been able to identify the two major GC signals (figure 5) as the $n$-methyl PS from condensation of neral and MEK and geranial and MEK, respectively. Also both isomethyl PS were identified using GC/MS. At this stage of our research, determination of the selectivity has not been carried out. Considering the obtained results in the citral–acetone condensation, similar selectivities in the citral MEK condensation can be expected. Analogous to DAA in the citral–acetone condensation, a substantial amount of self-condensation products of MEK was observed. In this case, leading to 4-hydroxy-3,4-dimethyl-2-hexanone and 3-hydroxy-3-methyl-5-heptanone, which were identified using GC/MS.

## 4. Conclusions

Our results demonstrate that the current activation procedure for HT-based solid-base catalysts has been significantly improved. When after rehydration water in the pores is replaced by ethanol, a high specific surface area remains preserved. This effect is connected with the considerably lower surface tension of the ethanol, which reduces the capillary forces in the HT stacks during evacuation of the solvent.

At 273 and 296 K the thus activated catalyst turned out to exhibit a high activity in the citral–acetone condensation as well as a high selectivity towards PS. Utilisation of this catalyst in the citral MEK condensation reaction at 296 K resulted in the formation of both $n$-methyl and isomethyl PS. These promising results show the potential of the activated HT-based catalyst in liquid-phase aldol condensations at low temperatures.

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